

KINETICS AND MECHANISM OF SOME VINYL RADICAL CYCLISATIONS

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Summary: The vinyl radicals **2a**, **2b**, and **11** each undergo fast *exo* ring closure to give **5a**, **5b**, and **12**, the first two of which readily rearrange to ring-expanded radicals.

Synthetic applications of vinyl radical ring closure have recently attracted considerable interest.¹⁻³ In contrast to suitably constituted alkenyl or alkenylaryl radicals which usually undergo highly regioselective ring closure in the *exo* mode,⁴ vinyl radical cyclisation often affords substantial yields of products containing the larger possible ring.^{2,3} The origin of this behaviour, which does not conform to expectation based on stereoelectronic considerations,⁴ has not yet been identified. It has been claimed to be neither kinetic nor thermodynamic.³ In an attempt to resolve this question and also to obtain kinetic data which have not previously been available for vinyl radical ring closures, we have now examined the behaviour of the radicals **2a**, **2b** and **11**.

The yields of products obtained when the bromide, **1a**, was heated in benzene with tributylstannane and a little azobisisobutyronitrile (AIBN) at 80° as initiator are given in Table 1. Since ring closure of the initially formed radical, **2a**, competes with its direct reduction by tributylstannane, the yield of the acyclic product, **3a**, should increase with increase in stannane concentration. The data in Table 1 show this to be so. However, the ratio of yields of the *exo* and *endo* products, 7%/6%, also increases with increase in stannane concentration. This phenomenon precludes direct formation of the two cyclised radicals, **5a** and **9a**, from the common intermediate, **2a**, but is consistent with a mechanism in which *exo* cyclization to give **5a** is followed by rearrangement of the latter to **9a** as illustrated in Scheme 1. In conformity with this mechanism direct formation of **5a** by treatment of the bromide **4a** with tributylstannane afforded a mixture of **6a** and **7a**.

Steady state treatment of the reactions of Scheme 1 gives $[C]_f = r \ln[(S_0+r)/(S_f+r)]$ where $[C]_f$ is the final total concentration of cyclized products, $[S]_0$ and $[S]_f$ are the initial and final concentrations of stannane, and r is the ratio of rate constants k_c/k_H . Table 1 shows that consistent values for this ratio were obtained when the

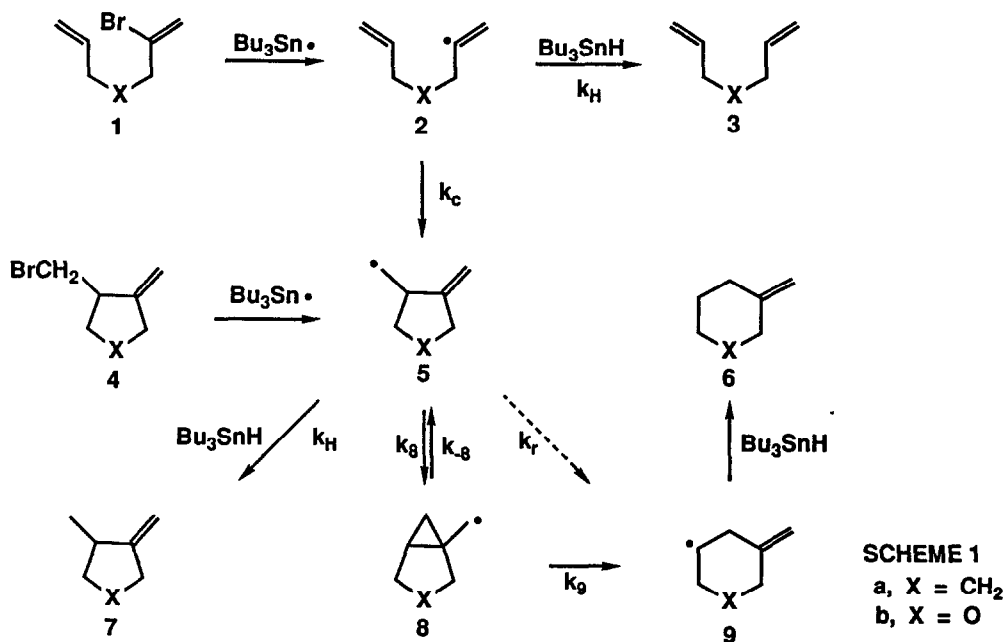


Table 1. Cyclisation of Vinyl Radicals in Benzene at 80°

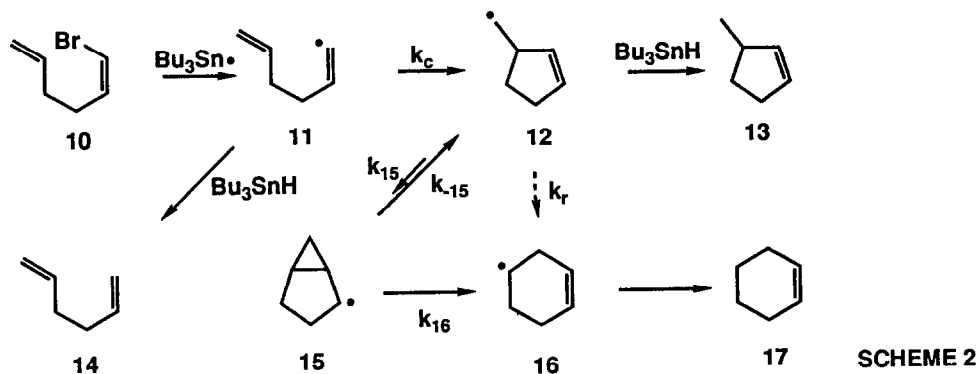
Precursor	[S] ₀	[S] _f	Products (yield %)	k_c/k_H	k_r/k_H'
1a	0.70 M	0.00 M	3a (47), 7a (38), 6a (15)	0.32 M	0.09 M
1a	0.50	0.00	3a (40), 7a (39), 6a (21)	0.32	0.10
1a	0.30	0.00	3a (28), 7a (42), 6a (30)	0.34	0.08
1b	0.70	0.00	3b (22), 7b (63), 6b (15)	1.12	0.05
1b	0.50	0.00	3b (17), 7b (62), 6b (21)	1.11	0.05
4a	0.30	0.27	7a (85), 6a (15)		0.05
4a	0.10	0.09	7a (61), 6a (39)		0.06
10	0.50	0.45	14 (32), 13 (65), 17 (3)	0.95	
10	0.30	0.27	14 (27), 13 (70), 17 (3)	0.77	

appropriate data were substituted into the above rate equation. Similar treatment of the yields of products from reactions at other temperatures gave the following typical values of k_c/k_H : 0.13 M (4°), 0.16 M (20°), 0.21 M (40°), 0.27 M (60°), and 0.42 (100°). Linear regression of these and similar data against 1/T gave values of log A and E_{act} (see Table 2).

The ratio of the rate constants k_r/k_H , where k_r is the rate constant for rearrangement of 5a into 9a was similarly obtained from the above equation in which $[C]_f$ now represents the normalised final concentration of the *endo* product 6a. The fact that similar values of k_r/k_H were obtained from reactions conducted with each of the bromides 4a and 1a lends credence to the proposed mechanism, and, in particular, suggests that direct *endo* ring closure of 2a to afford 9a does not occur. Since they were obtained more directly, the data obtained from reactions of 4a are probably the more reliable. Typical values of k_r/k_H obtained at different temperatures were: 0.012 M (20°), 0.021 M (40°), 0.027 (60°), 0.050 (80.6°).

A similar series of experiments was carried out with the vinyl bromide, 1b. In this case direct formation of the *exo* radical, 5b, by interaction of 4b with tributylstannane was not attempted, but the data presented in Table 1 indicate that the ratio of *exo* to *endo* product varies with stannane concentration and leave little doubt that the same general mechanism applies.

When the bromide, 10, was treated with tributylstannane the major products, 13 and 14, arose by *exo* cyclisation and direct reduction of the radical 11. The yield of the *endo* cyclisation product was very small, and at lower temperatures it became undetectable. In this case it was not possible to deduce whether the *endo* radical 16 arises by direct cyclisation of 11 or by rearrangement of 12. In either case the reaction is clearly very slow.



Values of k_c and k_r and their Arrhenius parameters were obtained from the data for k_c/k_H and for k_r/k_H by appropriate substitution for k_H and for k_H , using previous data for butyl radical⁵ and for 2,2-dimethylvinyl radical⁶ as models for reactions of radicals 5a and 5b, and of 2a, 2b and 11 respectively. The data in Table 2 show that the vinyl radicals 2a, 2b and 11 undergo *exo* ring closure very much more rapidly than hex-5-enyl radical, and with rate constants similar to those for analogous aryl radicals. As in both the hexenyl, and alkenylaryl series, incorporation of an oxygen atom in the chain, as in 2b, enhances the rate constant, presumably because the more favourable geometry lowers the strain energy of the transition state.⁴

Table 2. Arrhenius Parameters and Rate Constants

Reaction	$\Delta \log A$	ΔE_{act}	$\log A$ (s^{-1})	E_{act} (kcal.mol^{-1})	k (calc) at 60.0° (s^{-1})
2a \rightarrow 5a	1.0 ± 0.2	2.4 ± 0.25	10.7 ± 0.4	4.0 ± 0.5	1.2×10^8
2b \rightarrow 5b	0.9 ± 0.1	1.4 ± 0.1	10.6 ± 0.3	3.0 ± 0.4	4.3×10^8
11 \rightarrow 12	0.9 ± 0.4	1.6 ± 0.5	10.6 ± 0.5	3.2 ± 0.6	3.2×10^8
(4a \rightarrow) 5a \rightarrow 8a	1.8 ± 0.4	5.0 ± 0.9	10.9 ± 0.4	8.7 ± 0.9	1.6×10^5
(1a \rightarrow) 5a \rightarrow 8a	2.2 ± 0.2	5.2 ± 0.4	11.0 ± 0.3	8.9 ± 0.5	1.4×10^5
5b \rightarrow 8b	3.3 ± 0.2	7.5 ± 0.3	12.4 ± 0.4	11.2 ± 0.4	1.1×10^5

The kinetic data do not define the mechanism of rearrangement of 5 into 9. The most plausible route appears to be *via* formation of the cyclopropylcarbinyl system, 8, in which case $k_{\text{T}} = k_{\text{g}}[k_{\text{g}}/(k_{\text{g}} + k_{\text{g}})]$. Since k_{g} is probably smaller than k_{g} , we deduce that k_{g} has values similar to those given in Table 2 for k_{T} . Very probably k_{12} is of similar magnitude. However, in this case stereo-electronic factors disfavour ring opening to 16, and the most likely fate for 15 is to be reconverted into 12.

The observation that the initial *exo* products from vinyl radical cyclisation can undergo rearrangement to *endo* products⁷ has implications for the choice of experimental conditions for synthetic work. The formation of *endo* cyclisation products can be minimised by using low reaction temperatures and high stannane concentrations.

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- 7 After this work was completed we were informed by Professor G. Stork that he has reached a similar conclusion concerning the formation of *endo* cyclisation products.

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