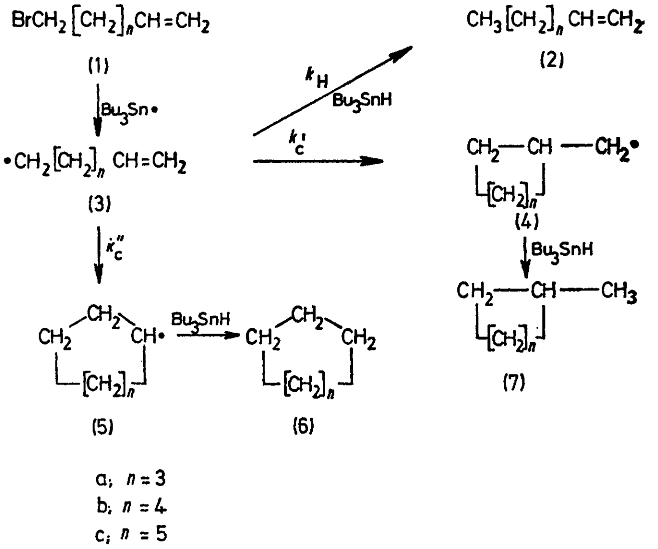
Intramolecular Addition in Hex-5-enyl, Hept-6-enyl, and Oct-7-enyl Radicals

By Athelstan L. J. Beckwith* and Graeme Moad
(*Organic Chemistry Department, University of Adelaide, Adelaide, South Australia* 5001)

Summary Each of the radicals, hex-5-enyl, hept-6-enyl, and oct-7-enyl, undergoes intramolecular addition preferentially in that direction which affords the cycloalkylcarbinyl radical, because both enthalpy and entropy factors are more favourable; an approximate rate constant for 1,5-hydrogen atom transfer in hept-6-enyl radical has been determined.

In an endeavour to identify the factors responsible for the unexpected[1,2] preferential formation of the less stable (**4a**) of the two possible products (**4a**) and (**5a**) of intramolecular addition in hex-5-enyl radical (**3a**)[1,3] we have determined the relative rates and temperature dependence of cyclization of the three ω-alkenyl radicals (**3a**—**c**).



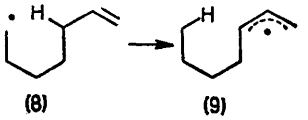
Scheme

The reactions expected to occur when a suitable bromoalkene is treated with Bu_3SnH in benzene, t-butylbenzene, or pentane are illustrated in the Scheme. 1-Bromohex-5-ene (**1a**) gave all three possible products (**2a**), (**6a**), and (**7a**), but cyclohexane (**6a**) was formed in very small yield. Only two products, oct-1-ene (**2c**) and methylcycloheptane (**7c**), were formed from 1-bromoct-7-ene (**1c**); however, the reaction with 1-bromohept-5-ene (**1b**) gave not only the expected olefinic (**2b**) and cyclic [(**6b**) and (**7b**)] products, but also *cis*- and *trans*-hept-2-ene, the formation of which is ascribed to the occurrence of the 1,5-hydrogen atom transfer process [(**8**) → (**9**)]. The allylic radical so formed should react with Bu_3SnH to give hept-1-ene and *cis*- and *trans*-hept-2-ene.[4] This was confirmed by a separate experiment in which 1-bromohept-2-ene and 3-bromohept-1-ene were treated with Bu_3SnH.

Application of steady-state theory to the proposed mechanistic scheme affords the integrated rate expression (1),[5] where Σk_C is the sum of the rate constants for cyclization processes, $\Sigma[C]$ is the total final concentration of

$$\Sigma[C] = \Sigma k_C/k_H\{\ln([S]_0+\Sigma k_C/k_H) - \ln([S]_F+\Sigma k_C/k_H)\} \quad (1)$$

cyclized products, and $[S]_0$ and $[S]_F$ are initial and final values respectively of $[Bu_3SnH]$. Since the hydrogen-atom transfer process [(**8**) → (**9**)] competes with the intermolecular reaction [(**3b**) → (**2b**)], Σk_C for hept-6-enyl radical (**3b**) includes the value of the rate constant for the former process, and $\Sigma[C]$ must include the final concentrations of hept-1-ene and hept-2-ene arising from that process.



(8) (9)

Reactions were conducted over a range of temperatures and initial stannane concentrations. Gas chromatographic analysis of the products allowed the calculation of k_C'/k_H and k_C''/k_H values of which at 65 °C are given in the Table together with values of $\Delta\Delta H^\ddagger$ and $\Delta\Delta S^\ddagger$, the differences between the activation parameters for cyclization and those for the reactions of the radicals (**3a**—**c**) with Bu_3SnH. Comparisons between the different systems may be made on the reasonable assumption that k_H, $\Delta H_H^\ddagger$ and $\Delta S_H^\ddagger$ have approximately the same values for each of the primary radicals (**3a**—**c**).[6]

Table

Kinetic data[a] for radical cyclization reactions

	(3) → (4)			(3) → (6)		
Radical	k_C'/k_H (65°)	$\Delta\Delta H^\ddagger$	$\Delta\Delta S^\ddagger$	k_C''/k_H (65°)	$\Delta\Delta H^\ddagger$	$\Delta\Delta S^\ddagger$
(**3a**)	0·218	12·3	23·8	0·0045	19·3	12·1
(**3b**)	0·0052	17·6	8·4	0·00089	21·8	5·9
(**3c**)	0·0015	24·7	0·4	$<10^{-5}$		

[a] $\Delta\Delta H^\ddagger = \Delta H_C^\ddagger - \Delta H_H^\ddagger$ (kJ mol^{-1}); $\Delta\Delta S^\ddagger = \Delta S_C^\ddagger - \Delta S_H^\ddagger$ (J/°).

Values of k_C'/k_H and k_C''/k_H decrease with increasing chain length of (**3**) because of increasingly unfavourable activation parameters. Within each system $k_C' >> k_C''$. The results clearly show the observed preferential formation of methylcycloalkanes is not due mainly to favourable entropy terms, as has been previously suggested.[7] The enthalpy term makes the more important contribution; reactions leading to the thermodynamically *less* stable products (**4a**—**c**) have *smaller* values of $\Delta H^\ddagger$ than those leading to cycloalkyl radicals (**5a**—**c**). These results support the hypothesis that the transition state for alkyl radical addition to an olefinic bond comprises a triangular array of centres lying in the same plane as that of the original π bond.[8]

These experiments also allow the approximate determination of the rate constant for 1,5-intramolecular hydrogen atom transfer in hept-6-enyl radical (**3b**). The value obtained ($k = ca.\ 5 \times 10^2\ s^{-1}$ at 25 °C) is considerably larger than that reported for the analogous process in saturated radicals.[9]

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