previously described for the reduction of **9** to **8**. The spectral data agreed with that reported[11] if their spectra of the separate compounds were superimposed on one another for comparison with the spectra recorded for the mixture.

proximal- **and** *medial,anti-***4-Methyl-1-spiropentylcarbinyl Tosylates (22-p and 22-m,a).** A mixture of the tosylates **22** was prepared from the corresponding alcohols in the manner described for the preparation of **10** from **8**.

After removal of the solvent the following spectral data for **22-p** and **22-m,a** were obtained: ir (neat) 3020 (w), 2970, 2930, 2900, 2850, 1595, 1490 (w), 1460, 1400 (sh), 1360, 1340 (sh), 1300 (w), 1290 (w), 1210 (w), 1190, 1180, 1130 (w), 1090, 1050, 1020, 940, 835, 820, 795, 775 cm^{-1}; nmr (100 MHz) complex multiplet from δ 4.26 to 3.76 (2 H), singlet at δ 2.43 (3 H), complex multiplet from δ 1.68 to 0.30 (9 H), the positions of the aromatic ring protons were not recorded because the HA-100 was locked on chloroform.

Acetolysis of *proximal-* **and** *medial,anti-***4-Methyl-1-spiropentylcarbinyl Tosylates.** A mixture of the tosylates **22-p** and **22-m,a** was solvolyzed in acetic acid at room temperature in the manner described for the acetolysis of **10**. After removal of the solvent, glpc indicated that the residue contained at least seven compounds. The four major components (ratio 8:2:1:2) were collected by preparative glpc on a 12 ft × 0.25 in. 20% LAC-2-R-446 column (T_c = 100°, F_c = 75 ml/min). The following spectral data were recorded. The compounds are listed in order of elution from the glpc column.

syn- **and** *anti-***5-Acetoxy-1-methylspirohexane (19-s and 19-a) (54%):** ir (CCl_4) 3056 (w), 2985, 2930, 2900 (sh), 2870 (w), 2850 (w), 1735, 1441, 1420 (w), 1367, 1347, 1230, 1188 (w), 1105, 1080, 1030, 888 (w) cm^{-1}; nmr (220 MHz) quintet (J = 7 Hz) at δ 5.11 (1 H), quintet (J = 7 Hz) at δ 4.99 (1 H), complex multiplet from δ 2.43 to 2.03 (8 H), singlet at δ 1.96 (6 H), overlapping doublets one (J = 7 Hz) centered at δ 0.96 and the other (J = 7 Hz) centered at δ 0.94 (total 6 H), complex multiplet from δ 0.73 to 0.45 (4 H), complex multiplet from δ 0.08 to −0.06 (2 H); exact mass 154.0992 (calcd 154.0994).

3-Acetoxy-2-cyclopropyl-1-butene (20) (18%): ir (CCl_4) 3085, 3003 (sh), 2981, 2932, 2970 (w), 1735, 1638 (w), 1442, 1422 (w), 1365, 1233, 1074, 1055, 1030, 1015, 945, 932, 892 cm^{-1}; nmr (220 MHz) quartet (J = 7 Hz) at δ 5.26 (1 H), broad singlet with fine splitting at δ 4.83 (1 H), broad singlet with fine splitting at δ 4.60 (1 H), singlet at δ 1.98 (3 H), doublet (J = 7 Hz) at δ 1.35 superimposed on a complex multiplet from δ 1.41 to 1.23 (total 4 H), complex multiplet from δ 0.72 to 0.62 (2 H), complex multiplet from δ 0.48 to 0.40 (2 H); exact mass 154.0992 (calcd 154.0994).

Unknown (9%): ir (CCl_4) 3035 (w), 2970, 2931 (sh), 2858, 1733, 1429, 1415 (w), 1368, 1353, 1308 (w), 1237, 1192, 1169, 1064 (sh), 1038, 1015, 969, 893 (w), 835 (w) cm^{-1}; nmr (220 MHz) complex multiplet from δ 5.35 to 5.20 (1 H), complex multiplet from δ 5.16 to 5.05 (1 H), complex multiplet from δ 2.52 to 2.44 (1 H), complex multiplet from δ 2.31 to 2.21 (2 H), complex multiplet from δ 2.21 to 2.14 (1 H), singlet at δ 1.95 (3 H), complex multiplet from δ 1.88 to 1.73 (2 H), complex multiplet from δ 1.61 to 1.52 (3 H); exact mass 154.0992 (calcd 154.0994).

1-Acetoxy-2-cyclopropyl-2-butene (21) (15%): ir (CCl_4) 3085 (w), 3006, 2932, 2915, 2858 (w), 1740, 1655 (w), 1440 (w), 1372, 1357, 1225, 1032, 1018, 954 cm^{-1}; nmr (220 MHz) quartet (J = 7 Hz) at δ 5.59 (1 H), singlet at δ 4.20 (2 H), singlet at δ 1.96 (3 H), doublet (J = 7 Hz) at δ 1.74 (3 H), complex multiplet from δ 1.51 to 1.38 (1 H), complex multiplet from δ 0.71 to 0.60 (2 H), complex multiplet from δ 0.71 to 0.60 (2 H), complex multiplet from δ 0.54 to 0.44 (2 H); exact mass 154.0986 (calcd 154.0994).

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Cyclization of 5-Hexenyl Radicals[1]

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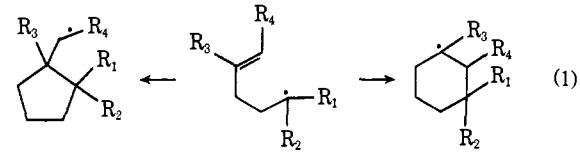
Abstract: The 5-hexenyl radical and its five 1- and 5-methyl-substituted derivatives have been generated by the radical chain reaction of the appropriate bromide and tributyl- or triphenylstannane. Cyclization to cyclopentylmethyl and cyclohexyl radicals competes with reaction of the uncyclized radical with stannane. Analysis of product yields as a function of stannane concentration and failure to detect open chain or cyclohexane products in the reaction of three cyclopentylmethyl bromides with stannanes or silanes indicate that cyclizations are irreversible under our conditions. At a given stannane concentration yields of cyclized products and ratios of six- to five-membered ring products both increase with temperature (40–100°) and with 1 substitution, while 5 substitution also increases the five- to six-membered ring ratio. Combination of our results with absolute rate data of Carlsson and Ingold indicates that 1 substitution slightly retards the rate of radical cyclization to cyclopentylmethyl products but increases the rate of cyclization to cyclohexyl products by a factor of at least 20. Accordingly, rather subtle steric effects as well as energetics determine the rate and direction of ring closure.

The cyclization of 5-hexenyl radicals has been the subject of a number of papers during the past 10 years[3] and is of interest because its ease and direction vary strikingly with radical structure. With highly substituted radicals (*e.g.*, R_1 = COOR, R_2 = CN) Julia has obtained chiefly cyclohexyl derivatives,[4] while several workers have observed that the unsubstituted



(1)

5-hexenyl radical cyclizes almost exclusively to the cyclopentylmethyl radicals[5] and a number of intermediate cases give both types of product.[3] The closure

(1) Taken from the Ph.D. thesis of A. Cioffari, Columbia University, 1971. Support of this work by a grant from the National Science Foundation is gratefully acknowledged.

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(3) For reviews, *cf.* M. Julia, *Pure Appl. Chem.*, **15**, 167 (1967); *Accounts Chem. Res.*, **4**, 386 (1971).

(4) M. Julia and F. Le Goffic, *C. R. Acad. Sci.*, **255**, 714 (1962).

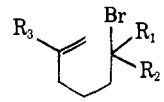
(5) (a) R. C. Lamb, P. W. Ayers, and M. K. Toney, *J. Amer. Chem. Soc.*, **85**, 3483 (1963); (b) C. Walling and M. S. Pearson, *ibid.*, **86**, 2262 (1964); (c) R. G. Garwood, C. J. Scott, and B. C. L. Weedon, *Chem. Commun.*, **1**, 14 (1965); (d) C. Walling, J. H. Cooley, A. A. Ponaras, and E. J. Racah, *J. Amer. Chem. Soc.*, **88**, 5361 (1966).

to a five-membered ring has been surprising since it is contrary to the usual direction of radical addition to double bonds and is energetically unfavorable both because of ring strain and the greater stability of secondary *vs.* primary radicals. More recently Julia[6] has shown that, at low temperatures, even highly substituted radicals give extensive closure to five-membered rings, a result for which three explanations are *a priori* possible: a lower activation enthalpy (but unfavorable entropy change) for the five-membered ring closure; reversibility of five-membered ring closure at higher temperatures; or, conceivably, a rearrangement (1,2 shift) of the substituted cyclopentylmethyl radical without actual ring opening. Julia[7] has found evidence for one of the latter two processes in the decomposition of peresters of 2-substituted cyclopentane acetic acids to give varying yields of five- and six-membered ring products although no open chain olefinic products were detected. On the other hand, no evidence of ring opening or rearrangement has been detected for the simple cyclopentylmethyl radical under the conditions where cyclization of the 5-hexenyl radical has been observed.[5a,d]

In 1966 we reported[5d] a convenient technique for studying radical cyclizations *via* the reaction of the appropriate alkenyl halide with tributylstannane as developed by Menapace and Kuivila[8] which has the advantage that the lifetime of the intermediate radicals may be systematically varied by changing the stannane concentration. This paper describes application of this technique to a systematic study of a series of alkyl-substituted 5-hexenyl radicals, which serves to clarify the effect of structure on both rate and direction of ring closure. In the accompanying paper[9] we consider the reactions of the 1-phenyl-5-hexenyl radical where reversibility and rearrangement become important processes.

Results and Discussion

Reactions with tributylstannane and triphenylstannane were examined for 6-bromo-1-hexene and its five possible 2- and 6-methylated derivatives. Reactions



	R_1	R_2	R_3
1	H	H	H
2	H	H	CH_3
3	CH_3	H	H
4	CH_3	H	CH_3
5	CH_3	CH_3	H
6	CH_3	CH_3	CH_3

were run in sealed, degassed tubes in benzene solvent using azobisisobutyronitrile (AIBN) initiator at 40 and 70° and di-*tert*-butyl peroxide (DTBP) at 100° and above and either equivalent concentrations of alkenyl bromide and stannane or excess bromide. Actual yields of cyclized and uncyclized products were determined by gas–liquid chromatography (glc) and ranged from 85 to 100%, but, for presentation and analysis, all have been normalized to 100% to show relative product yields. Results are summarized in Tables I–VI which give the range of stannane concentrations employed and the resulting range of product compositions. Each experiment represents the result of two (or more) runs and product ratios were also determined in duplicate (or more) at a number (usually three) of intermediate concentrations. Yields of cyclized products increased smoothly with decreasing initial stannane concentration and all data were used in the calculations below, except as noted.

Analysis of our data is based upon the following reaction scheme. First, we assume that the halide re-

Table I. Reduction of 6-Bromo-1-hexene (**1**) by Tributylstannane

$[R_3SnH]_0$[a]	T, °C	Yield, %[c]		
0.512	40	64.0	36.0	
0.0251	40	10.0	90.0	Trace
0.512	70	56.0	43.0	
0.0251	70	8.8	90.1	1
0.512	130	45.0	55.0	
0.0251	130	6.8	92.1	1.1
0.573[b]	70	80.3	19.7	
0.0287[b]	70	24.0	76.0	
0.573[b]	130	70.8	29.2	
0.0287[b]	130	14.6	85.4	

[a] Approximately 50% excess RBr in all experiments. [b] Triphenylstannane. [c] Yields 85–98% normalized to 100%.

Table II. Reduction of 6-Bromo-2-methyl-1-hexene (**2**) by Tributylstannane

$[R_3SnH]_0$[a]	T, °C	Yield, %[c]		
0.500	40	62.1	37.9	
0.050	40	21.2	76.8	2.0
0.500	70	56.1	42.4	1.5
0.050	70	17.6	80.0	3.4
0.500	100	50.6	46.6	2.8
0.050	100	13.9	81.5	4.6
0.500[b]	100	73.1	25.4	1.5
0.050[b]	100	28.2	67.8	4.0

[a] Equivalent RBr in all experiments. [b] Triphenylstannane. [c] Actual yields 85–95% normalized to 100%.

Table III. Reduction of 6-Bromo-1-heptene (**3**) by Tributylstannane

$[R_3SnH]_0$[a]	T, °C	Yield, %[c]		
0.500	40	58.6	41.4	
0.020	40	10.9	88.0	1.1
0.500	70	52.3	47.2	
0.020	70	8.7	88.4	2.9
0.500	100	43.7	53.7	2.6
0.020[d]	100	6.1	88.6	5.1
0.500[b]	100	73.8	25.2	1.4
0.020[b]	100	18.5	77.4	4.1

[a] Equivalent RBr in all experiments. [b] Triphenylstannane. [c] Actual yields 85–95% normalized to 100%. [d] Trans isomer.

(6) M. Julia and M. Maumy, *Bull. Soc. Chim. Fr.*, 2321 (1967).
(7) M. Julia, M. Maumy, and L. Mion, *ibid.*, 2641 (1967).
(8) L. W. Menapace and H. G. Kuivila, *J. Amer. Chem. Soc.*, **86**, 3047 (1964).
(9) C. Walling and A. Cioffari, *ibid.*, **94**, 6064 (1972).

Table IV. Reduction of 6-Bromo-2-methyl-1-heptene (4) by Tributylstannane

$[R_3SnH]_0$[a]	T, °C	Yield, %[c]		
				 [d]
0.500	40	55.7	39.0	5.6
0.020	40	11.1	75.8	13.1
0.500	70	51.5	42.5	6.0
0.020	70	7.9	76.8	15.3
0.500	100	37.6	50.7	8.2
0.020	100	4.5	74.3	21.2
0.250[b]	100	49.9	41.9	8.2
0.020[b]	100	15.0	66.4	18.6

[a] Equivalent RBr in all experiments. [b] Triphenylstannane. [c] Actual yields 85–95% normalized to 100%. [d] Cis:trans ratio 9:1.

Table V. Reduction of 6-Bromo-6-methyl-1-heptene (5) by Tributylstannane

$[R_3SnH]_0$[a]	T, °C	Yield, %[c]		
				
0.500	40	57.2	33.9	8.9
0.025	40	10.1	81.5	8.4
0.500	70	50.1	36.7	14.2
0.025	70	7.0	79.8	13.2
0.500	100	27.6	50.6	21.8
0.025	100	4.1	92.2	23.7
0.500[b]	100	58.0	32.6	13.4
0.025[b]	100	11.1	65.5	24.4

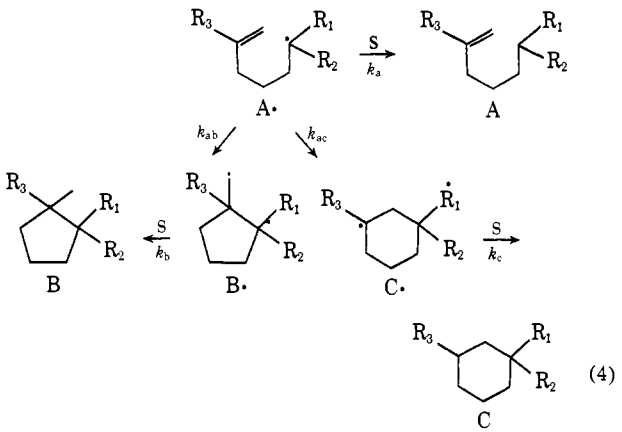
[a–c] For corresponding footnotes see Table II.

duction is a long-chain process with the propagating steps

$$R\cdot + R_3SnH \longrightarrow RH + R_3Sn\cdot \quad (2)$$

$$R_3Sn\cdot + RBr \longrightarrow R_3SnBr + R\cdot \quad (3)$$

and, second, that the cyclizations are irreversible and no rearrangement occurs between cyclized radicals. The competing steps which determine product ratios are then given by the scheme shown in eq 4. Here A,



(4)

B, and C represent uncyclized, cyclopentyl, and cyclohexyl derivatives and S the stannane. Making use of the usual steady-state assumptions and recognizing that the rate of consumption of S is equal to the total rate of formation of A, B, and C give the differential equation

$$-\frac{d([B] + [C])}{d[S]} = \frac{k_{ab} + k_{ac}}{k_a[S] + k_{ab} + k_{ac}} \quad (5)$$

Table VI. Reduction of 6-Bromo-2,6-dimethyl-1-heptene (6) by Tributylstannane

$[R_3SnH]_0$[a]	T, °C	Yield, %[c]		
				
0.500	40	55.0	23.1	21.9
0.025	40	8.9	47.1	44.0
0.500	70	42.5	24.3	33.2
0.025	70	5.4	46.9	47.7
0.500	100	25.6	27.6	46.8
0.025	100	4.1	37.4	58.5
0.500[b]	100	55.1	18.2	26.7
0.025[b]	100	8.1	37.7	54.2

[a–c] For corresponding footnotes see Table II.

Making the substitution $(k_{ab} + k_{bc})/k_a = r$ and integrating from $[S] = [S]_0$ to $[S] = 0$ gives the desired expression for the yield of cyclized product.

$$([B] + [C])/[S_0] = \ln (r + [S]_0)/[S]_0 \quad (6)$$

If the scheme is correct, each experiment in a set should give the same value for r[10] and also a constant ratio of $k_{ac}/k_{ab} = [C]/[B]$. Analysis of our data showed that these conditions were obeyed at higher initial stannane concentrations in all systems, but that in some one or both ratios drift at the lowest concentrations employed. Possible origins of this drift are considered later. Table VII gives values or r and $[C]/[B]$ in the range where both are sensibly constant, so that we can assume that we are examining essentially irreversible cyclizations. Our results with the unsubstituted 5-hexenyl radical at 40° are in good agreement with those reported earlier,[5d] but data at higher temperatures are now consistent with eq 6 and we have been unable to confirm the deviations which led us to propose a more complex process.[5d] Additional evidence that we are indeed dealing with the simple irreversible radical chain postulated is that r's for triphenylstannane system at 70–130° are consistently $1/(3.6 \pm 0.5)$ those for tributylstannane, in good agreement with a relative reactivity of 4.2 for these stannanes toward *tert*-butyl radicals at 25° reported by Carlsson and Ingold.[11] Ratios of k_{ac}/k_{ab} are also in agreement for the two stannanes. Further, a competitive experiment in which 0.5 *M* *n*-hexyl bromide and 0.5 *M* 6-bromo-1-hexene were treated with 0.5 *M* tributylstannane gave a product mixture containing 51.4% *n*-hexane showing that the reactivity of 6-bromo-1-hexene in reaction 3 is normal for a primary bromide with no evidence for participation of the double bond.

Considering next the effect of substitution on cyclization of 5-hexenyl radicals, the data of Table VII lead to the following generalizations. (1) For all radicals, yields of cyclized products increase with temperature. (2) At constant temperature, yields of cyclized products increase with increasing stability of the initial radical: primary < secondary < tertiary. (3) Ratios of 6-/5-membered ring products also increase with temperature and with initial radical stability: primary < secondary < tertiary. (4) For each initial radical type, ratios of six-/five-membered ring products are higher for R_3 = Me than for R_3 = H. These conclusions can be ana-

(10) The quantity r for any experiment must be determined by successive approximation, most conveniently by a computer technique.

(11) D. J. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, **90**, 7047 (1968).

Table VII. Summary of Rate Constant Ratios in Cyclization of 5-Hexenyl Radicals

Radical	T, °C	$[S]_0$	r[b]	k_{ac}/k_{ab}[b]
	40	0.512–0.025	0.107 ± 0.006	<0.005
	70	0.512–0.05	0.153 ± 0.008	≤0.01
	130	0.512–0.05	0.256 ± 0.006	≤0.02
	70	0.573–0.029[a]	0.042 ± 0.001	<0.005
	130	0.573–0.029	0.078 ± 0.002	<0.005
	40	0.5–0.05	0.099 ± 0.012	≤0.027
	70	0.5–0.05	0.132 ± 0.023	0.040 ± 0.004
	100	0.5–0.05	0.193 ± 0.041	0.055 ± 0.004
	100	0.5–0.05[a]	0.058 ± 0.001	0.060 ± 0.002
	40	0.5–0.1	0.130 ± 0.012	≤0.011
	70	0.5–0.1	0.178 ± 0.005	≤0.03
	100	0.5–0.1	0.273 ± 0.010	0.047 ± 0.002
	100	0.5–0.1[a]	0.064 ± 0.004	0.047 ± 0.01
	40	0.5–0.1	0.150 ± 0.003	0.13 ± 0.01
	70	0.5–0.1	0.211 ± 0.027	0.15 ± 0.01
	100	0.5–0.1	0.331 ± 0.030	0.19 ± 0.03
	100	0.25–0.1[a]	0.096 ± 0.005	0.21 ± 0.02
	40	0.5–0.1	0.150 ± 0.009	0.21 ± 0.04
	70	0.5–0.1	0.235 ± 0.039	0.36 ± 0.03
	100	0.5–0.1	0.592 ± 0.077	0.45 ± 0.04
	100	0.5–0.1[a]	0.153 ± 0.018	0.41 ± 0.03
	40	0.5–0.1	0.160 ± 0.010	0.91 ± 0.04
	70	0.5–0.1	0.275 ± 0.023	1.28 ± 0.08
	100	0.5–0.1	0.575 ± 0.132	1.61 ± 0.09
	100	0.5–0.1[a]	0.156 ± 0.013	1.58 ± 0.11

[a] Triphenylstannane (tributylstannane in all other experiments). [b] Experimental error is standard deviation from mean for all experiments within range of $[S]_0$ given.

lyzed further (at least on a semiquantitative basis) by combining them with the absolute rate constant measurements of Carlsson and Ingold.[11] In a comprehensive and elegant investigation of stannane reductions, they have reported rate constants for the reaction of tributylstannane with *n*-hexyl, cyclohexyl, and *tert*-butyl radicals at 25° of 1×10^6, 1.2×10^6, and 0.74×10^6, respectively. As they note, the cyclohexyl radical result is anomalous and may represent either experimental uncertainty or some peculiarity of cyclic radicals. However, if we assume that the rates of reaction of our primary and tertiary radicals with tributylstannane at 40° are approximately the same as theirs at 25°, we may calculate the rate constants for cyclization shown in Table VIII. The results are rather surprising. Substitution at the double bond slightly decreases k_{ab} (five-membered ring closure), a plausible steric effect, and increases k_{ac} by a factor of 2.7 or more as would be expected since six-membered ring closure now yields a tertiary radical. However, going from a primary to a tertiary initial radical only decreases k_{ab} by 20–30% and most of the change in product ratios arises from a large *increase* in k_{ac}. *A priori* one might have anticipated that the increased yield of six-membered ring products as one goes from primary to tertiary radicals would be the consequence of a large drop in rate for five-membered ring cyclization and a slower decrease in six-membered ring cyclization, since this should be the thermodynamically more stable product. Although our calculations are only approximate, they certainly indicate that this is not the case. In fact, for it to be so the ratios of k_a's for primary:tertiary would have to be over 20:1 rather than 4:3 as indicated by Carlsson and Ingold's results. We see no obvious detailed rationalization for this apparent increase in k_{ac} with radical complexity. The now well-established tendency for simple radicals to cyclize preferentially to five-membered rings also remains mysterious, although examination of molecular models indicates that, if usual bond lengths and angles are retained, overlap between the odd electron and the π-electron system of the double bond occurs most easily nearer C-5 than C-6.

Table VIII. Estimated Rate Constants for Cyclization of 5-Hexenyl Radicals

Radical	k_{ab}, $sec^{-1} \times 10^{-5}$	k_{ac}, $sec^{-1} \times 10^{-5}$
	1.1	<0.005
	0.9	≤0.024
	0.92	0.19
	0.62	0.54

Two other points are worth noting. First, both cyclizations yielding stereoisomeric products give preferentially the more stable isomer, although in one, cyclization of the 1-methyl-5-hexenyl radical to 1,2-dimethylcyclopentane (Table II), stereochemistry is fixed at the time of ring closure while in the other, cyclization of the 1,5-dimethyl-5-hexenyl radical to 1,3-dimethylcyclohexane (Table III), stereochemistry is not determined until the cyclized intermediate reacts with stannane. Second, variation of product yields with temperature shows that, in general, $\Delta H_a^{\ddagger} < \Delta H_{ab}^{\ddagger}$

Chart I

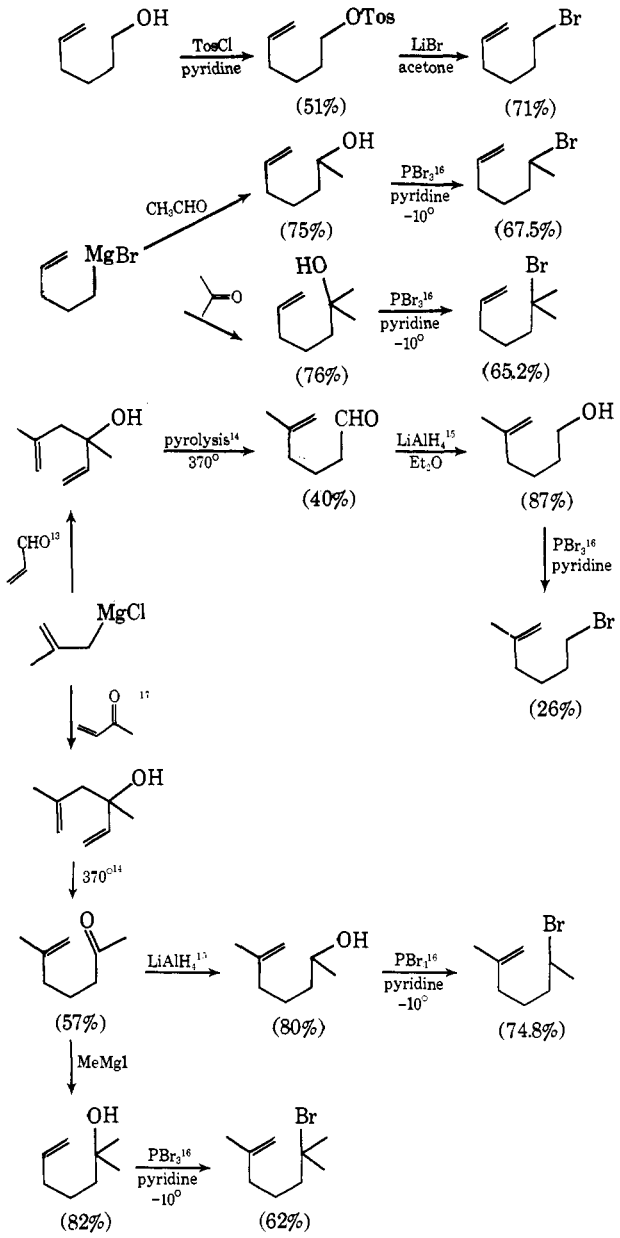
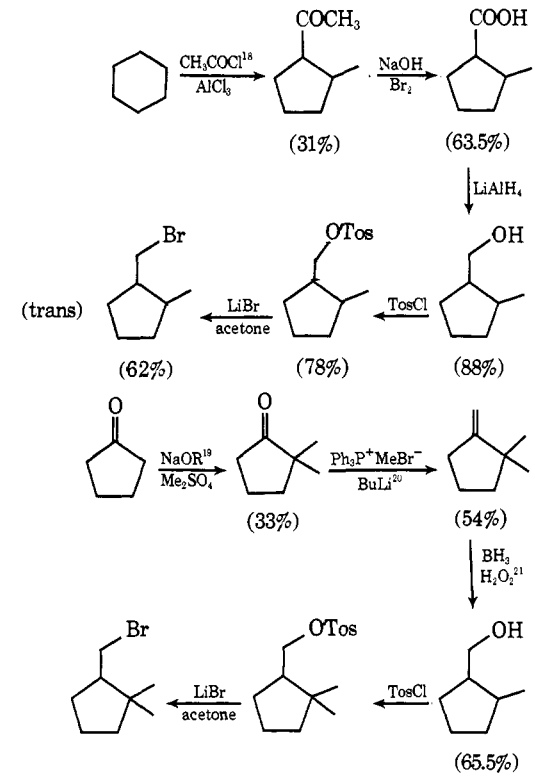


Chart II



$< \Delta H_{ac}^{\ddagger}$, although differences are rather small. Thus, the effects of structure on rate deduced from Tables VII and VIII become even larger at higher temperatures. Incidently, the data also indicate that Arrhenius A factors for the cyclizations are similar to those for the displacement step given by k_a. Since such displacements commonly have A factors of 10^{10}–10^{11}, values for these cyclizations are abnormally low[12] presumably reflecting a large entropy loss on cyclization.

Finally we must consider our results at very low stannane concentrations where calculated values of r and $k/_{ac}k_{ab}$ both drift. The obvious possibility is reversibility of cyclization or other rearrangement of cyclized radicals. This has been ruled out for the unsubstituted 5-hexenyl radical and we have now tested two other cases. Reduction of 2-methyl- and 2,2-dimethylcyclopentylmethyl bromides with tributylstannane at 40° gave only unrearranged hydrocarbon (78–92%) and no detectable yield (<0.1%) of either the corresponding olefins or methylcyclohexanes. Reduction with triethylsilane (which is less reactive and should accordingly give longer radical lives) again gave 75–85% unrearranged product and no methylated cyclohexanes (olefin would not be expected since silanes add readily to olefinic double bonds). Since the amount of reversibility or rearrangement required to accommodate our drifts in rate constant ratios should have given significant amounts of rearranged products, we can only conclude that they have some other origin. As noted, actual yields of reported products were 85–100%, and some of the difficulty could be preferential loss of one or another cyclized radical to other products, *e.g.*, addition to benzene solvent at very low stannane concentration.

The tests just described thus support our interpretation that our higher concentration experiments were indeed on irreversible systems in which products are under kinetic control. The accompanying paper, however, considers a case where both reversibility and rearrangement can be clearly demonstrated.[9]

Experimental Section

Materials. All reactants, solvents, and reference compounds were either commercial materials purified by conventional methods and physical constants and purity checked before use or were synthesized by straightforward methods. The substituted **6-bromo-1-hexenes** were prepared as shown in Chart I,[13-17] Superscript numbers give literature procedures (for the same or similar compounds) followed. Preparation of substituted **cyclopentylmethyl bromides**

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is shown similarly in Chart II.[18-21] Purity of all final compounds was checked by glc and also nmr and ir spectra. **Stannanes** were prepared by $LiAlH_4$ reduction of the corresponding commercial chlorostannanes.[22] They were stored in benzene solution under argon at −20° until used.

Cyclizations were carried out in sealed, degassed tubes, using reagent concentrations indicated in Tables I–VI in benzene solvent containing AIBN (40 and 70°) or DTBP (100 or 130°) initiator and internal standard for subsequent analysis (*n*-hexane for C_6 compounds, *n*-heptane for C_7, and naphthalene for C_8 and C_9). Experiments were run to completion: 24 hr at 40°, 6 hr at 70°, and 3 hr at 100°.

Product analyses were carried out by glc using didecyl phthalate on 60–80 firebrick columns at 95–120°. In every system products were identified by collection and determination of physical properties as well as comparison of retention time with authentic standards. Cyclohexane and methylcyclohexane were obtained in such low yield that they were determined by retention time alone. Authentic materials were also used for calibration of the internal standards employed.

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Interconversion of 1-Phenyl-5-hexenyl, 2-Phenylcyclopentylmethyl, and 3-Phenylcyclohexyl Radicals[1]

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Abstract: Reaction of either 6-bromo-6-phenyl-1-hexene or *trans*-2-phenylcyclopentylmethyl bromide with tributylstannane yields 6-phenyl-1-hexene (A), *trans*-1-methyl-2-phenylcyclopentane (B), and phenylcyclohexane (C) showing that the three corresponding radicals are interconvertible under these conditions. Further, the product ratio C/A is much higher in the second case indicating direct rearrangement of the 2-phenylcyclopentylmethyl radical to 3-phenylcyclohexyl without ring opening. Thus, this system provides the first clear-cut case of an intramolecular 1,2-alkyl shift in a monoradical rearrangement. The B → C rearrangement is also reversible since some B is formed starting with 3-bromo-1-phenylcyclohexane. *cis*-2-Phenylcyclopentylmethyl bromide similarly yields A, B, and C in addition to unrearranged hydrocarbon and the indan derivative arising from intramolecular radical attack on the aromatic ring. Here, product distributions indicate that A, B, and C arise solely by ring opening.

In our preceding paper[3] we examined the cyclization of a series of methyl-substituted 5-hexenyl radicals generated *via* the radical chain reaction between tributyl- or triphenylstannane and the appropriate alkenyl bromide[4] and concluded that, under our conditions, there was no evidence for reversibility of the cyclizations observed. This paper describes a similar study of the 1-phenyl-5-hexenyl radical where it was anticipated that resonance stabilization would increase the likelihood of observing reversibility of the cyclization process.[5]

Results

Experiments were carried out in sealed, degassed tubes using benzene as solvent, varying concentrations of tri-*n*-butylstannane, equivalent 6-bromo-6-phenyl-1-hexene, and azobisisobutyronitrile (AIBN) or di-*tert*-butyl peroxide (DTBP) as initiator. Reactions were run to complete consumption of stannane and gave 85–95% yields of olefin and cyclized products. Results (see Scheme I) appear in Table I with all yields normalized to 100%. During each run, stannane concentration varied from its initial value to zero. Since for later discussion product distributions over more limited

Table I. Reduction of 6-Bromo-6-phenyl-1-hexene by Tributylstannane

		Yield, %		
$[R_3SnH]$	*T*, °C	A	B	C
0.500	70	27.4	56.8	15.8
		(43.2)	(51.3)	(5.5)
0.250	70	11.6	62.3	26.1
		(15.7)	(65.6)	(18.7)
0.100	70	5.5	57.3	37.2
		(8.3)	(64.9)	(26.8)
0.050	70	2.7	49.7	47.6
		(3.3)	(53.5)	(43.2)
0.025	70	2.1	45.9	52.0
		(2.5)	(50.4)	(47.1)
0.010	70	1.5	39.2	59.3
0.500	100	17.4	53.8	28.8
		(26.3)	(56.7)	(17.0)
0.250	100	8.5	50.9	40.6
		(11.6)	(54.8)	(33.6)
0.100	100	3.8	45.0	51.2
		(5.1)	(53.0)	(41.9)
0.050	100	2.5	37.0	61.5
		(3.9)	(40.3)	(55.8)
0.025	100	1.1	33.7	66.2
		(1.4)	(34.6)	(64.0)
0.010	100	0.6	32.3	77.1

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