

CYCLIZATION OF 4-(1-CYCLOHEXYNYL)BUTYL RADICAL¹



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In an attempt to delineate the factors affecting the direction of radical cyclization we have studied the reactions of 4-(1-cyclohexenyl)butyl radical (V) generated from the appropriate peroxide (IV)³ or from 4-(1-cyclohexenyl)butyl bromide (I).³ The results of the reaction of the bromide (I) with tributyltin hydride (Table I) support the view^{4,5} that the sole initial process is the generation of the radical (V) and are consistent with the proposed reaction scheme.

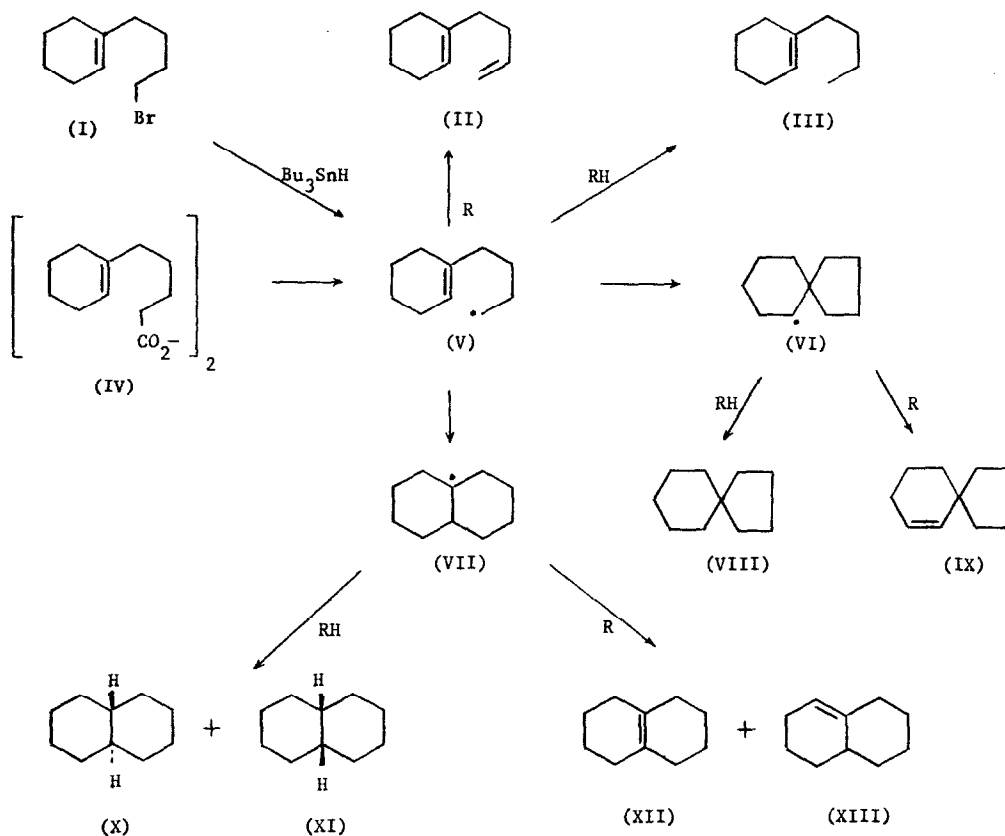
TABLE I. Products from Reaction of 4-(1-Cyclohexenyl)butyl Bromide (RBr) with Tributyltin Hydride (R'₃SnH) in Benzene

RBr =	0.04M	0.02M	0.20M	0.10M
R' ₃ SnH =	0.02M	0.028M	0.10M	0.14M
 ^a	35	43	61	78
 ^a	36	31	21	12
<u>trans-decalin</u> ^a	24	22	15	9
<u>cis-decalin</u> ^a	4.3	3.8	2.7	1.5
total yield ^b	93	102	91	103
cyclized products ^a	64	57	39	22
<u>1,5-cyclization</u> total cyclization x 100	56	57	54	54
<u>cis-decalin</u> trans-decalin x 100	17.9	17.3	18.0	16.7

^a Moles per 100 moles of total products ^b % of theoretical based on starting materials

The absence of products arising from dimerisation or disproportionation (e.g., IX, XII, XIII) reflects the great ease of hydrogen-atom abstraction from R₃SnH, and the constancy of the relative yields of spiro compound (VIII) and decalins (X, XI) over a seven-fold change in hydride concentration indicates that product formation via concerted cyclization and

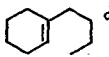

hydrogen-atom transfer⁴ is unimportant. Similarly the constancy of the cis:trans-decalin isomer ratio, and its similarity to that previously observed^{6,7} suggests that the decalyl radical formed in our experiments has a sufficiently long lifetime to assume either of its possible configurations.⁷ Thus we are unable to deduce the stereochemistry of the decalyl radical (VII) immediately after completion of the cyclization process.⁸



The reaction mixtures obtained by thermolysis of the peroxide (IV) were more complex (Table II), and included olefins (XII, XIII) formed by disproportionation.⁹ However, within the limits of the method, the results support the proposed mechanistic pathways.

In both sets of experiments approximately 50% of cyclised products were formed via the thermodynamically less favourable route. This result, which accords with previous observations^{4,10-12} indicates that radical cyclization is largely under stereoelectronic control, and that the transition state, presumably, is sterically different from that in comparable cationic cyclization reactions which usually proceed to the 6-membered ring systems.^{13,14}

TABLE II. Products from Thermolysis of Bis 5-(1-cyclohexenyl)butanoyl Peroxide^a

Solvent	cyclohexane		benzene		benzene/cumene ^b	
total yield ^c	20	31	25	34	38	37
 ^d	28	27	44	40	39	37
 ^d	34	38	23	25	21	23
<u>trans-decalin</u> ^d	17	17	7.8	10	6.2	6.7
<u>cis-decalin</u> ^d	3.5	3.4	2.2	2.5	2.1	2.4
1,9-octalin ^d	4.7	5.4	11	13	14	14
9,10-octalin ^d	1.9	2.0	4.5	3.7	11	9
$\frac{\text{cis-decalin}}{\text{trans-decalin}} \times 100$	20.5	20	28	25	34	36
$\frac{1,5\text{-cyclization}}{\text{total cyclization}} \times 100$	56	57	48	46	39	41

^a Concentration of peroxide = 0.15M^b Cumene concentration = 0.6M^c % of theoretical based on peroxide^d Moles per 100 moles of total products

Little is known about the intimate structure of the transition state for homolytic addition to the double bond.¹⁵ It is often assumed that formation of the transition state involves maximum overlap of the unpaired electron with the occupied π orbital but the results of cyclization experiments are difficult to rationalize in terms of this concept. Examination of models leads us to suggest that the initial stages of the addition process involve interaction of the unpaired electron with the lowest unoccupied orbital of the π system and that the approach of the radical centre occurs preferably within the plane of the π system and along a line extending almost vertically from one of the terminal carbon atoms. Our view that bond formation will occur at the terminus of the olefinic linkage most readily approached vertically by the radical rationalizes not only the preferred formation of 5-membered rings, but also the ready cyclization of 6-heptenyl systems,¹¹ and the inability of the 4-pentenyl system to undergo ring formation.¹²

References

- 1 Project supported by the Australian Research Grants Committee.
- 2 National Research Council Postdoctoral Fellow. Present address: Canada Department of Agriculture, Research Station, Lethbridge, Alberta, Canada.
- 3 The two radical precursors were prepared by unambiguous syntheses from cyclohexanone following a general route devised for the preparation of related compounds by one of us (G.E.G.).
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