

S U M M A R Y

P A R T 'A'

MECHANISM OF REARRANGEMENT OF LONGIFOLENE
TO ISOLONGIFOLENE

CHAPTER I: Elucidation of Terpene Rearrangements Using
Deuterium Labels

The use of deuterium labels in elucidating the mechanism of rearrangements among terpenes has been reviewed. The versatility of this method in resolving varied mechanistic problems has been brought out.

CHAPTER II: Mechanism of Rearrangement of Longifolene to
Isolongifolene

The sesquiterpene hydrocarbon longifolene (1,5,5-trimethyl-11-methylenetricyclo[5,3,1.0^{6,10}]decane) on exposure to strong acids undergo a deep seated molecular rearrangement to isolongifolene (2,2,7,7-tetramethyltricyclo[6,2,1,0^{3,8}]undec-3-ene). The mechanism of rearrangement has been elucidated by effecting the isomerization of longifolene with $\text{BF}_3 \cdot \text{Et}_2\text{O} \cdot \text{AcOD}$ and it has been shown that longicyclene (1,5,5,11-tetramethyltetracyclic[6,2,1,0^{6,10},0^{7,11}]undecane) is not an intermediate in the formation of isolongifolene. Longifolene-4,4,5-5-d₄ was synthesized and isomerized to isolongifolene-d₄, which was shown to be isolongifolene-1,2,4,4-d₄, by converting the latter to some of its

suitable derivatives. This study provides experimental proof in favour of the mechanism proposed by Benson *et al.* involving 5,2-exo-methyl migration, instead 3,2-endo methyl migration proposed earlier.

P A R T 'B'

SOME TRANSFORMATIONS IN ISOLONGIFOLENE
SERIES

CHAPTER I: 'Steric Diversion' in Electrophilic Additions

Electrophilic addition of halogens and pseudo-halogens to isolongifolene has been studied. It does not give normal addition products. Instead, ^{it gives} a mixture of substitution product (8-haloisolongifolene) rearranged product (3-haloneoisolongifolene, i.e. 4,4,11,11-tetramethyl-7-halotricyclo [5,2,1,0^{3,8}] undec-2-ene). In case of chlorine, significant amount of 8-chlorocycloisolongifolene (2,2,7,7-tetramethyl-4-chlorotetracyclo [5,2,1,0^{3,8},0^{3,9}]undecane) is also formed. The term 'Steric Diversion' has been suggested for all such cases, where deviation from normal addition products occurs due to steric reasons.

CHAPTER II: Structure of an Acetate from Solvolysis
8-Haloneoisolongifolene

8-Haloneoisolongifolene on refluxing with NaOAc-AcOH gives a tertiary acetate (45%), whose structure has been shown to be 4,4,9,9-tetramethyl-8-acetoxytricyclo[5,2,2,0^{5,8}]undec-2-ene, by incisive application of spectroscopic (mass, PMR, NMR, LSR) studies and its chemical transformations.

CHAPTER III: A Novel Fragmentation Reaction and Its
Applications

A novel fragmentation reaction of homoallylic alcohols; of type $\begin{array}{c} \text{C} \\ | \\ \text{C}=\text{C}-\text{C}-\text{C}-\text{OH} \end{array} \rightarrow \begin{array}{c} \text{C} \\ | \\ \text{C}=\text{O} \end{array} + \text{X}-\begin{array}{c} \text{C} \\ | \\ \text{C}-\text{C}-\text{C} \end{array}$ (where X = Cl, OH), is demonstrated. Homoallylic alcohols on treatment with chlorine undergo cleavage to allylic chloride and carbonyl fragments. A similar cleavage occurs during acid catalysed oxirane ring opening of the corresponding epoxide. Synthesis of sesquiterpene alcohol, secolongifolene diol (2,2,6-trimethyl-7-hydroxymethyl-9-exo-(2'-hydroxyethyl)bicyclo[4,2,1]non-1-ene) is described.