The Carbonium Ion Theory of Whitmore which has already been invoked in this thesis to explain several reactions, namely, the isomerisation of 3-carene to menthadienes, the aromatisation of 3-carene to p- and m-cymenes, the dehydration of terpineol to p-menthadienes and the cracking of α-pinene to various aromatics and olefins, appears to be capable of a more general application in the field of terpenoid reactions. Some of the terpenoid reactions other than those examined in the thesis to which the carbonium ion mechanism has been utilised are the Wagner, Meerwein and Nametkin rearrangements, isomerisation of α-pinene to p-menthadienes, polymerisation of β-pinene with aluminium chloride, formation of 1-ethyl-2-isopropyl-cyclopentene from pinene in presence of dilute aqueous salt solutions, cyclisation of geraniol to dipentene and conversion of isoprene to geraniol, α-terpineol, terpineol-4, and 1:4-cineole.

5. Roberts and Day, ibid. 1950, 72, 1228.
Now a literature survey shows a large number of hydrogen ion catalysed reactions of monocyclic, bicyclic and acyclic penoids for which either no mechanism or no satisfactory mechanism seems to have been given. An attempt is made in this section to apply the carbonium ion theory to typical reactions ongoing to these three groups of terpenoids.

Before doing so, it may be of interest to indicate briefly the main features of the formation and typical reactions of carbonium ions applicable to the reactions discussed.

**Carbonium Ions.**

**Definition**— In an ionic (heterolytic) cleavage of a covalent bond between two atoms X and Y, one of them (X) loses an electron which it furnished in establishing the covalent bond with Y and thereby acquires a unit positive charge. When

\[
\begin{align*}
\text{X}:\text{Y} \quad \longrightarrow & \quad \left[ :\text{X} \right]^+ + \left[ :\text{Y} \right]^- \\
\text{as a carbon atom, the ion} \quad \left[ -\text{C}^+ \right] \text{ which has only six electrons in the valence shell, is called a carbonium ion. Or in other words, in the formation of a carbonium ion there is a decomposition of the type:}
\end{align*}
\]

\[
\begin{align*}
-\text{C} \quad \longleftrightarrow \quad -\text{C}^+ + :\text{Z}^- \\
\text{Alexander, 'Principles of Ionic Organic Reactions', (John Wiley & Sons, Inc., N.Y.) 1950, pp.34,41.}
\end{align*}
\]
Formation of carbonium ions:— Carbonium ions may be
med from:

(a) unsaturated compounds\(^1\text{-}\text{3}\) by the addition of a proton from an acid reagent:

\[
\text{>C} : \text{C} < + \text{H}^+ \Leftrightarrow \text{>C} : \text{C} < + \text{H}
\]

(b) alcohols\(^1,2\) by the addition of a proton from an acid reagent to an unshared electron pair of the hydroxyl oxygen, decomposition of the resulting addendum ion:

\[
\text{OH} + \text{H}^+ \Leftrightarrow \text{R} : \text{O} - \text{H} \Leftrightarrow \text{R}^+ + \text{O} - \text{H}
\]

and (c) cyclopropanes\(^4,5\) by the opening of the 3-membered ring with acceptance of a proton from an acid reagent:

\[
\begin{align*}
\text{CH}_3 & + \text{H}^+ \Leftrightarrow \text{CH}_3\text{-CH}_2\text{-C}^+ \\
\text{CH}_3
\end{align*}
\]

References:

Pines, Huntsman and Ipatieff, J. Amer. Chem. Soc. 1951, 73, 4343; 1953, 75, 2311.
Most of the carbonium ion reactions can be best explained if it is assumed that tertiary carbonium ions form most readily, and are most stable; secondary next, and primary next, so that the order of stability of these very unstable fragments is as follows: tertiary $>^1$ secondary $>^2$ primary $>^3$. This order of stability of the carbonium ions has been confirmed on theoretical grounds by Eavans and Polanyi$^3$.

Reactions of carbonium ions$^{1,2}$:—When a carbonium ion is set free by one of the processes just considered, a great variety of reactions is possible. The carbonium ion may:

(a) lose a proton from an adjacent carbon atom to form a multiple linkage:

\[
\begin{align*}
\text{–C} : & \text{H} \\
\text{\downarrow} & \\
\text{–C}^+ & \text{\leftrightarrow} \\
\text{\downarrow} & \\
\text{–C} & \text{+ H}^+
\end{align*}
\]

This change is often referred to as the expulsion of a proton from a carbonium ion.

(b) isomerise by shift of an electron pair with its attached proton:

\[
\begin{align*}
-C: & :H & \sim H: & \leftrightarrow & -C^+: & \sim C & -H \\
-C^+ & & & & \sim C & -H
\end{align*}
\]

This change is often referred to as the hydride ion shift ($\sim H^-$). A new carbonium ion is thus formed with the charge on the atom which was once the adjacent carbon atom.

and (c) attach itself to a base, i.e., to any substance carrying an unshared electron pair:

\[
\begin{align*}
\text{n-Bu}^+ & + & \begin{cases} H & \\ :O & -H \\ \vdots & \vdots \\ :O & \text{NO} \end{cases} & \rightarrow & \begin{cases} H & \\ :O & -H \\ \vdots & \vdots \\ :O & \text{NO} \end{cases} \\
\text{n-Bu}^- & - & \begin{cases} - \text{Bu} & -\text{Cl} \\ - \text{Bu} & -\text{ONO} \end{cases}
\end{align*}
\]

The Beta Rule: When a carbonium ion carbon atom takes a pair of electrons intramolecularly, that pair of electrons always comprises one of the bonds beta to the original carbonium.

---

ion carbon. The beta rule is the rule of least rearrangement since it involves the shifting of electrons only:

\[ H_2C: C::C:C::C:R \rightarrow H_3C::C::C::C:R + C::C:C:R \]

In applying carbonium ion mechanism to terpenoids it is convenient to classify them under monocyclic, bicyclic and acyclic compounds, and to subdivide the reactions of each group further into isomerisation, dehydration, hydrochlorination, hydroxylation and cyclisation.

**Monocyclic Compounds.**

**Isomerisation:**

**p-Menthenes:** It has been reported by Frank and Berry\(^1\) that 3\((9)\)-p-methene (I) isomerises under the influence of acid catalysts into 4\((8)\)- and 3-p-methenes (III and V). This transformation consists essentially in the addition of a proton from the acid catalyst to the pi electrons of the double bond in (I) to give the C\(_3\) carbonium ion (II) which can by the expulsion of a proton from the C\(_4\) atom result in 4\((8)\)-p-methene (III), or by an hydride ion shift go over into the isomeric carbonium ion (IV), this by expulsion of a proton giving 3-p-methene (V).

---

The same mechanism applies with suitable modifications to the obtention by the same authors of 8 (9)- and 3-p-menthenes from 4 (9)-p-menthene by refluxing with 30% ethanolic sulphuric acid.

**Dihydrocarvone:**—The isomerisation of dihydrocarvone (VI) to carvenone (IX) achieved by Wallach\(^1\) with dilute sulphuric acid, by Baeyer\(^2\) with concentrated sulphuric acid, by Klages\(^3\) with formic acid and by Muller\(^4\) with hydrochloric acid can be explained by the following sequence of reactions:

\[ \text{CO} \xrightleftharpoons{\text{H}^+} \text{CO} \xrightleftharpoons{\sim \text{H}^+} \text{CO} \xrightleftharpoons{\text{H}^+} \text{CO} \]

\[ \text{VI} \quad \text{VII} \quad \text{VIII} \quad \text{IX} \]

---

2. Baeyer, Ber.1904,27,1921.
p-Menthadienes: Wallach isomerised dipentene\(^1\) (X) and terpinolene\(^2\) (XIV) into \(\alpha\) - and \(\gamma\) -terpinenes (XIII and XIV) with acid catalysts. The mechanism for this transformation involving addition of proton to the parent substance with a subsequent shift of hydride ion and expulsion of proton is illustrated as follows:

\[
\begin{align*}
X & \xrightarrow{H^+} \text{XI} & \xrightarrow{H^-} \text{XII} & \xrightarrow{H^+} \text{XIII} & + \\
& \xrightarrow{H^+} \text{XIV}
\end{align*}
\]

The transformation of \(\alpha\) - phellandrene (XVI) into the isomeric \(\alpha\) - and \(\gamma\) -terpinenes (XIII and XIV) with ethanolic sulphuric acid\(^1\) involves first the formation of carbonium ion (XVII), which then suffers an hydride ion shift to give, with subsequent expulsion of a proton, \(\alpha\) - and \(\gamma\) -terpinenes:

p-Menthaatrienes:- Menagerene, \(\Delta^{1,5;4(8)}\)-p-menthaatriene (XVIII) has been reported to isomerise on treatment with dilute sulphuric acid into p-cymene (XXI)\(^1\). This, as can be seen from the following reactions, involves merely the addition of a proton followed by a hydride ion shift and expulsion of a proton:

Dehydration:

Menthol:- Menthol (XXII) can be dehydrated into 3-p-methene (V) by the action of very dilute sulphuric acid\(^2\), the

---

yield being over 90%. From the viewpoint of carbonium ion mechanism, the first step in this process is the abstraction of the hydroxyl group from menthol (XXII) through the acceptance of a proton from the acid catalyst resulting in the elimination of a water molecule and the formation of secondary carbonium ion (XXIII); this isomerises via a hydride ion shift to the more stable tertiary carbonium ion (IV) which with expulsion of a proton gives 3-p-menthene (V). It may be remarked that since the secondary carbonium ion, being less stable than the tertiary, rapidly passes into the latter, it does not favour the expulsion of a proton from the C₂ position to give 2-p-menthene, as has been experimentally observed.

α-terpineol: The dehydration of α-terpineol (XXIV) by various acid catalysts at different concentrations to p-menthadienes such as terpinolene (IV), α-terpinene (XIII) and sometimes

Wallach, Ann.1907, 356, 249; 1909, 368, 11;
Esayer, Ber.1894, 27, 447;
dipentene (I) involves first the abstraction of the hydroxyl group from α-terpene through the acceptance of a proton from the acid catalyst, resulting in the elimination of a water molecule and the formation of the carbonium ion (II). This suffers expulsion of a proton either from the C₄ atom to yield terpinolene (IV) or from C₁₀ atom yield dipentene (X). As for the formation of α-terpinene (XIII), reference may be made to what has been said in the case of p-menthadiene.

![Chemical Structures]

Carveol—The dehydration of carveol (XV) to p-cymene (XXI) with warm dilute sulphuric acid¹ is easily explained by the following scheme of reactions:

p-Menthan-2:4-diol: Wallach\(^1\) dehydrated p-menthan-2:4-diol (XXX) by digestion with oxalic acid and obtained carvenol (XXXIII) and \(\alpha\)-terpinene (XIII), and probably the isomeric alcohol (XXXIV). This transformation may be explained as involving the initial formation of the carbonium ion (XXXI) which then by expulsion of a proton gives carvenol (XXXII) or the isomeric alcohol (XXXIV). \(\alpha\)-terpinene (XIII) may be accounted for by the formation of the carbonium ion (XXXIII) from carvenol, its isomerisation by an hydride ion shift to the more stable tertiary carbonium ion (XXXIV) and subsequent elimination of a proton. These are indicated in the following equations:

\[
\begin{align*}
\text{XXX} & \xrightleftharpoons{H^+(-H_2O)} \text{XXXI} \\
\text{XXXII} & \xrightleftharpoons{-H^+} \text{XXXIII} \\
\text{XXXIV} & \xrightleftharpoons{H^+(-H_2O)} \text{XXXV} \\
\text{XIII} & \xrightleftharpoons{-H^+} \text{XXXIV}
\end{align*}
\]

Bicyclic Compounds.

Isomerisation:

\[ \alpha\text{-Thujene and } \delta\text{-Sabimene:} - \] The isomerisation of \( \alpha\text{-thujene} (\text{XXXVI}) \) to \( \alpha - \) and \( \delta - \)terpinenes (XIII and XIV) brought about by treatment with dilute ethanolic hydrochloric acid\(^1\) starts with the formation of the carbonium ion (XXXVII) which then suffers break-up of the cyclopropane ring in accordance with the beta-bond fission rule to yield the carbonium ion (XII), from which expulsion of a proton as has already been explained leads to \( \alpha - \) and \( \delta - \)terpinenes.

\[ \text{XXXVI} \quad \xrightarrow{H^+} \quad \text{XXXVII} \quad \leftrightarrow \quad \text{XII} \quad \xrightarrow{H^+} \quad \text{XIII} \quad + \quad \text{XIV} \]

It is to be noted that this explanation seems to be simpler and more elegant involving as it does the known behaviour of carbonium ion than the apparently ad hoc mechanism recently

suggested by Menon. It may be of interest to remark that the isomerisation of d-sabinene (XXXVIII) to α- and γ-terpinenes can be explained by the addition of a proton to the exocyclic methylene group resulting in carbonium ion (XXXVII) which can undergo the aforementioned transformations to give the final products.

Pinocarvone:— The possibility of the formation of carvone (XLII) from pinocarvone (XXXIX) in presence of dilute acids is illustrated by the following reactions in which the beta-bond fission plays an important part as in the previous example:

\[
\begin{align*}
\text{XXXIX} & \xrightarrow{H^+} \text{XL} & \text{XL} & \xrightarrow{-H^+} \text{XLII} \\
\end{align*}
\]

3-Carene:— It may be recalled that the isomerisation of 3-carene (XLIII) by dilute sulphuric acid into dipentene (X), γ-terpinene (XIV), sylvestrene (XLV) and isocarvestrene (XLVI)

and by salicylic acid into $\alpha$-terpinene (XIII), terpinolene (IV) and sylvestrene (XLVI) involves essentially the two-directional fission of the cyclopropane ring in the presence of $H^+$ with the formation of carbonium ions (XI and XLIV), these in turn undergoing the usual carbonium ion reactions to yield the above menthadienes:

A similar mechanism would account for the isomerisation of $\Delta^4$-carene in the presence of acid catalysts.

Carone:— The isomerisation of carone (XLVII) into carvenone (IX) using concentrated sulphuric acid may be represented by the following equations:

1. Semmler and Schiller, Ber. 1927, 60B, 1591.
2. Rimini, Gazzetta, 1909, (ii), 68, 112.
When the 3-carbon ring of thujone (XLVIII) is broken by heating with 40% sulphuric acid, an isomeric ketone, 'isothujone' (I) is formed, which change is represented by Wallach and Semmler as follows:

However, this isomerisation can be explained by the carbonium ion theory, and involves the fission of the cyclopropane ring of thujone (XLVIII) with acceptance of a proton from the acid catalyst to give the carbonium ion (II), which then undergoes an hydride ion shift and expulsion of proton to give 'isothujone'.

2. Semmler, Ber. 1900, 33, 275.
Dehydration:

**Pinocarveol:** The dehydration with consequent aromatisation of pinocarveol (LIII) to p-cymene (XXI) by means of sulphuric acid is explicable on the basis of the initial formation of carbonium ion (LIV) which then isomerises with the fission of beta bond to the carbonium ion (XXVI), this latter after the usual hydride ion shift and expulsion of proton etc., leading to p-cymene (XXI) as has already been shown in the case of carveol.

\[ \text{LIII} \xrightarrow{\text{H}^+} \text{LIV} \xrightarrow{\text{H}^+} \text{XXVI} \xrightarrow{\text{H}^+} \text{XXVII} \]

\[ \text{XXVIII} \xleftarrow{\text{H}^+} \text{XXIX} \xleftarrow{\text{H}^+} \text{XI} \]

**Sabinol:** The dehydration of sabinol (LV) to p-cymene (XXI) under the influence of halogen acid can be accounted in a similar manner:

2. Fromm, Ber.1898, 21, 2030; 1900, 33, 1209.
Hydrochlorination:

2-Carene: The formation of dipentene and sylvestrene monohydrochloride (LVII and LX) and dihydrochlorides (LIX and LXII) on hydrochlorination may be represented by a carbonium ion mechanism as follows:

Kondakov and Schindelmeiser reported the formation of carvestrene dihydrochloride (LXII) by prolonged treatment of fenchyl alcohol (LXIII) with hydrogen chloride. Semmler represented the transformation by the following scheme:

The Wagner rearrangement is assumed to occur with the intermediate formation of a tricyclic hydrocarbon (LXV), which is now known to be incorrect.

An alternative mechanism for this conversion based on the carbonium ion theory is as follows:

\[ \text{Hydroxylation:} \]

Sabinene: Wallach\(^2\) obtained terpine-4-ol (LXXI) by hydration of sabinene (XXXVIII) with mineral acids, and the conversion was assumed to take place with the intermediate formation of sabinene hydrate (LXX):

Hovever, the mechanism based on the carbonium ion theory presented in the following scheme explains the same transformation without the postulation of the intermediate sabinene hydrate:

\[
\text{XXXVIII} \quad \xrightarrow{H^+} \quad \text{XXXVII} \quad \xrightarrow{\text{H}_2\text{O}} \quad \text{LXXI} + H^+
\]

Sabinol: When sabinol (LV) is shaken with 5% sulphuric acid, ring fission occurs and \(\Delta\)-p-menthene-4:6-diol (LXXII) is formed. The following mechanism explains the experimental observations:

\[
\text{LV} \quad \xleftrightarrow{H^+} \quad \text{LVI} \quad \xleftrightarrow{\text{H}_2\text{O}} \quad \text{XXVII} \quad \xrightarrow{H^+} \quad \text{LXXII}
\]

Isopulegol:— The hydration of isopulegol (LXXIII) to p-menthane-3:8-diol (LXXV) with dilute sulphuric acid\(^1\) may be represented by the following scheme:

\[
\begin{align*}
\text{LXXIII} & \xrightarrow{H^+} \text{LXXIV} \xleftarrow{H_2O} \text{LXXV} + H^+ \\
& = \text{Acyclic Compounds.}
\end{align*}
\]

Cyclisation:

Geraniolene:— The cyclisation of geraniolene (LXXVI) by sulphuric acid to \(\alpha\)-, \(\beta\)-, and \(\gamma\)-cyclogeraniolenes (LXXX, LXXXI, and LXXXI) which formed the subject of the investigations by several authors\(^2\) can be accounted in the following manner:

\[
\begin{align*}
\text{LXXXVI} & \xrightarrow{H^+} \text{LXXXVII} \rightleftharpoons \text{LXXXVIII} \\
& \xrightarrow{-H^+} \text{LXXXIX} + \text{LXXX} + \text{LXXXI}
\end{align*}
\]

---

2. Tiemann and Semmler, Ber. 1893, 26, 2724; Tiemann, ibid. 1900, 33, 3711; Wallach and Franke, Ann. 1902, 324, 114; Escourrou, Bull. Soc. chim. 1926 (iv), 39, 1460; 1928 (iv), 43, 1277.
Reasonable explanations of a large variety of hydrogen ion catalysed terpenoid reactions have been given based on the accepted principles of carbonium ion behaviour.