INTRODUCTION
The presence of isopropenyl and isopropylidene forms having ethylenic double bonds in the 1(2) and 2(3) positions respectively is quite common with most of the terpenoids. Ascertaining the nature of this double bond in natural terpenoids aroused considerable controversy and until the recent years the problem was unresolved. The chemical method for the determination of the position of the double bond is based on oxidation experiments whereby acetone being expected from an isopropylidene form and formaldehyde from an isopropenyl group (1,2).

\[
\begin{align*}
\text{HCHO} & \quad 4 \\
\text{H} & \\
\text{O} & \\
\text{H}_3\text{C} & \\
\text{CH}_3 & \\
\text{R} & \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \\
& \quad \text{R} \quad \text{C} \quad \text{C} \quad \text{C} \\
\text{H} & \\
\text{O} & \\
\text{H}_3\text{C} & \\
\text{CH}_3 & \\
\text{R} & \text{C} \quad \text{C} \quad \text{C} \\
& \quad \text{R} \quad \text{C} \quad \text{C} \\
\text{H} & \\
\text{O} & \\
\text{H}_3\text{C} & \\
\text{CH}_3 & \\
\text{R} & \text{C} \quad \text{C} \quad \text{C} \\
& \quad \text{R} \quad \text{C} \quad \text{C} \\
\text{H} & \\
\text{O} & \\
\text{H}_3\text{C} & \\
\text{CH}_3 & \\
\end{align*}
\]

This procedure is, however, reported to be associated with certain ambiguities since on ozonolysis many such terpenoids yield both acetone and formaldehyde indicating
thereby the presence of the mixtures of both isopropylidene and isopropenyl groupings (1). But there are evidences which show that the terpenoids are structurally homogeneous and the anomalous results appear due to partial rearrangements during experimental conditions (1-3). A typical example is that of citronellol (1), which on ozonolysis was said to give both acetone and formaldehyde in proportions indicating a ratio of isopropylidene form (a) to isopropenyl form (b) of about 4:1. Another classical instance is quoted by Kuhn and Roth (4) who observed that the ultra violet curves of two crystalline cis and trans isomeric dehydrogeranic acid (c) were incompatible with the presence of 30 per cent of less conjugated isopropenyl form (d) which was determined by the ozonolytic experiments(4,5).

This tautomeric shifting of the double bond is also observed when the oxidation is conducted with different
reagents under different experimental conditions. For instance, while the oxidation of α-santalyl malonic acid (e) by alkaline potassium permanganate solution gave the keto acid (f), ozonolysis of the same, yielded the aldehyde (g) (6). This was explained (6) on the basis of a postulation that in a neutral solution the above acid (e) exists as (ea) while in the alkaline medium a facile tautomerism occurs converting (ea) into (e).

The difficulty encountered in settling such anomalies in the case of terpenoids is accentuated by the fact that the majority of terpenes are liquids of questionable purity. Moreover those few cases where solid or crystalline derivatives have been obtained, also appear to be mixtures. On the basis of chemical evidence, it is generally argued that in terpenoids, especially acyclic and monocyclic, one of the double bonds is present both in the isopropenyl and isopropylidene forms. However, due to hyperconjugation the double bond in isopropylidene form should be more stable as compared to the isopropenyl form. The chemical evidence also
shows that in several natural terpenoids such as isopulegone (h), perillaldehyde ((i), carvone (j), limonene (k), ocimene (l) etc. the isopropenyl forms are preponderant. Owing to these ambiguous results, the oxidative degradation, therefore, as an unequivocal method of structure diagnosis of this type of olefinic linkages is not free from suspect (7-10).

In recent years, the physical methods of structure determination, such as infrared absorption spectroscopy, has made possible to settle this long disputed problem of the two types of olefinic groupings by showing characteristic infrared absorption bands for the isopropylidene and isopropenyl forms (11-14). This technique permits detection of even minor structure variations and also a degree of analytical and structure control in the synthetic work. The nature of various kinds of olefinic linkages can be ascertained by this method.
Use of ultraviolet spectroscopy in the field of terpenoids has greatly helped particularly in the detection of conjugation. Empirical rules proposed by Woodward (15) and modified by Fieser (16) are available for predicting the position of maxima of the high intensity absorption bands of such system as conjugated dienes, trienes and conjugated ketones etc. Absence of conjugation may also be detected by determining the spectrum of the coloured complexes or compounds obtained on treatment with tetranitromethane and 2,4-dinitrophenylhydrazine respectively.

The use of nuclear magnetic resonance spectroscopy particularly in fixing up location and surroundings of the proton has further helped in the determination of detailed molecular structure (17). Nuclear magnetic resonance spectroscopy is a more powerful tool than ultraviolet and infrared spectroscopy in terms of structural information derived from the spectrum. The method can not, however, replace these older methods, instead it is complimentary to them. From the knowledgeable use of the three, a great deal of structural information about a molecule can be obtained. Raman spectra (18) has also been used in the determination of structure of organic compounds though to a limited extent. The use of mass spectroscopy (19) and X-ray analysis (20,21) for complex structures is gaining importance. Encouraging progress has also been made in unravelling the stereochemistry of terpenoids by the application of the principles of conformational
analysis (22), molecular rotation relationship (23,24) and optical rotatory dispersion (25,26).

The physical tools have proved to be of great help in the establishment of complete structural anatomy of a natural terpenoid. The question of the terminal unsaturation in the terpene field having been solved, the final and rigorous confirmation of its constitution is sought through a synthesis by an unambiguous method and comparing the spectral data of the synthetic product with that of the natural one. To achieve this target for the synthesis of individual terpenoids literature records a steady improvement in the methods, for the creation of isopropylidene, isopropenyl and other olefinic linkages. Some of the methods for the formation of olefinic linkages are namely, dehydration of alcohols (27,28), submission of acetates (29-31), boric esters (32), xanthates (33,34) and tosylates (35,36) to pyrolysis. But all these techniques invariably involve isomerisation under the conditions employed for the execution of these procedures. The decarboxylation of olefinic acids is limited to the formation of styrenes and stilbenes (37,38). The method of Hofmann degradation for the introduction of double bond also involves circuitous route and drastic experimental conditions (39). A recent procedure involving the conversion of mercaptans to the terminal olefins with one additional carbon atom has also been reported (40).

A primary consideration in the successful synthesis of terpenoids having terminal unsaturation in isopropenyl or
isopropylidene chain, is the conditions employed in such synthesis. To achieve the synthesis of the individual terpenoid in a particular pure form and without any ambiguity, in the present investigations, one of the routes employed is the well known Wittig reaction (41) and modified Wittig reaction (42).

It was shown by Wittig and Schollkopf (41) that alkylidene and arylidene triphenylphosphoranes prepared by the action of suitable base on an alkyl or aryltriphenylphosphonium halide, react rapidly with aldehydes and ketones to form olefins. The Wittig reaction is usually assumed to proceed via the four membered complex. Wittig and others (43-45) postulated the first intermediate to be betaine (A).

\[
\begin{align*}
(C_6H_5)_3P^+ & \xrightarrow{C(R)_2} (C_6H_5)_3P^+ C(R)_2 \\
\text{(c6H5)}_3P & \xrightarrow{C(R)_2} (c6H5)3P \rightarrow O+(R)_2 \text{C} \equiv \text{C(R)}_2 \\
\text{(SCHEME-I)}
\end{align*}
\]
It would seem that the formation of betaine (A) i.e. electrophilic attack of the ylid carbon by the carbonyl carbon (scheme I) is not the only route, an alternate pathway, e.g., nucleophilic attack on the ylid phosphorus by the carbonyl oxygen (scheme II); which course the reaction takes, depends upon the steric and electronic factors as well as upon the environments. Conformational analysis shows that if the reaction between the phosphorylid and carbonyl begins with nucleophilic attack on the phosphorus, trans olefins should result, whereas electrophilic attack upon the ylid carbon leads to both cis and trans olefins (45).

Bases and solvents commonly employed (44) include butyl and phenyl lithium in ether, benzene and tetra-hydrofuran or lithium alkoxides in corresponding alcohols or dimethyl formamide. Corey et al (46) have reported the use of dimethylsulphoxide as solvent in the presence of sodium hydride as base for better yield of olefins in the Wittig reaction. Thus, the yield of methylene cyclohexane obtained by Corey (46) is twice that obtained by Wittig (41). Camphor, a rather unreactive ketone presents no special problem when dimethylsulphoxide is used as solvent. In addition these conditions allow highly selective reaction with ketonic function when both ketone and ester are present in the same molecule (46).
Wittig olefin synthesis has wide application with outstanding success in many fields e.g., carotenoids, steroids, vitamins, polyenes, heterocyclic compounds and sugars (47). This reaction has also been utilised in the synthesis of terpenic alkaloids (48). In the field of terpenoids some unambiguous and remarkable synthesis have been achieved with the application of this reaction. Recently this technique has been exploited to achieve the elegant synthesis of (±) kaur-16-en-19-oic acid (49) norsqualene (50), β-cubebene (51) and α-t-cadinene (52).

Very recently Japanese workers successfully employed this synthetic tool in achieving the synthesis of phytone (53) an intermediate ketone for the synthesis of α-tocopherol. The sequence of reactions is depicted by the following diagrams.
Vig et al. also exploited this technique in the synthesis of various mono-, and sesquiterpenoids (54-63) including β-farnesene (64) which is diagramatically depicted below:

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{C} & \quad \text{H}_3\text{C} \\
\text{CO} & \quad \text{CH}_3 & \quad \text{CO} & \quad \text{CH}_3 \\
\text{H}_3\text{C} & \quad \text{C} & \quad \text{H}_3\text{C} & \quad \text{CH}_2\text{CHO} \\
\text{H}_3\text{C} & \quad \text{C} & \quad \text{H}_3\text{C} & \quad \text{CH}_3
\end{align*}
\]

**Phytone**

Vig et al. also exploited this technique in the synthesis of various mono-, and sesquiterpenoids (54-63) including β-farnesene (64) which is diagramatically depicted below:
The reaction of phosphonate-carbanions (B) in modified Wittig reaction (42) with ketones and aldehydes to produce olefins proceeds smoothly under mild conditions to give fair to excellent yield of olefins. Indeed, this synthesis is a very useful supplement to well known Wittig reaction. The phosphonate carbanions have a number of advantages over the triaryl-phosphorane or Wittig reagent. They are in most cases less expensive and react with a wider variety of ketones and aldehydes, usually under mild conditions and are not sensitive to atmospheric oxygen. It has also been reported (65) to invariably furnish a great preponderance of trans olefin.

The mechanism of trans olefin formation is similar to that proposed by Bergelson and Schemyakin (45) for the Wittig reaction of carbethoxy methylene triphenylphosphorane with aldehydes and ketones. The reaction of carbethoxy methylene triphenyl-phosphorane (C) with benzaldehyde yields only trans cinnamic ester. The specifically trans directed reaction of the ylid (C) may be explained by the electron density distribution in the ylid.
The deficiency in electron density at the ylid carbon atom hinders electrophilic attack by the carbonyl carbon so that nucleophilic attack on the ylid phosphorus by the carbonyl oxygen becomes more probable. Of the two possible conformations for the resultant dipolar ions the preferred one is (E) leading to the more stable four membered ring (F_a) and thence to the trans isomer. The lower energy of the transition state (E) as compared to (D) is firstly due to the less steric interactions of the substituents and secondly to the circumstances that only in the case of (E) can there be maximum overlap of \( \pi \)-electrons of the carbethoxy and phenyl groups, developing ethylenic bonds (coplanarity factor) (65).
The important application of modified Wittig reaction is provided by the recently reported synthesis of a branched chain sugar (66) which is present in some recently discovered antibiotics.
Mayer et al. utilized this reaction for the total synthesis of Rhodoxanthin, a carotenoid, which is schematically depicted below:

\[
\begin{align*}
R &= \text{H} \\
\text{p} &= \text{p-Cl-C}_6\text{H}_4-\text{CO-}
\end{align*}
\]

(67)

\[
\text{(CH}_3\text{)}_2\text{P=CH-CO}_2\text{CH}_3
\]

\[\text{t-BuOK, DMF}\]

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This important synthetic tool has also been successfully exploited for the synthesis of terpenic compounds e.g., dl-nuciferal (68), all-trans violet leaf alcohol (69), dl-humbertiol (70) and β-sinensal (71). Synthesis of β-sinensal has been achieved through the following sequence of reactions.
Another equally potential approach for the formation of isopropenyl and isopropylidene groups, is the hydrogenolysis reaction (72-76) of suitably constituted allylic carbinols with sodium and ethanol in liquid ammonia. The reaction sequence can be generalised in the following steps.

Birch investigated a number of vinyl carbinols (72) and expressed the view that the hydrogenolysis of vinyl carbinols such as geraniol (I) takes place by way of the anion (II).
On the assumption that the anion forms part of the transition state, its ease of formation which must be greater, the greater the stability of the charge in the mesomeric system, probably decides whether or not hydrogenolysis can occur. The experimental evidence with these mesomeric carbanions shows that proton addition occurs at the centre of highest charge density (77, 78) (i.e. the least alkylated end of the ion), e.g.,

The conversion of Sabinol (III) to α-thujane (IV) and of (V) into (VI) are the other examples which show that the addition occurs at the least alkylated end of the ion (75).
Since the carbanion in the transition state is mesomeric, so it does not matter to a first approximation, whether the hydroxyl group attached is primary or secondary. For instance, conversion of geraniol and linalool leads into the same hydrocarbon methylgeraniolene.

The identity of the product in this case gives clear indication that the mesomeric system is involved in the transition state.

Vig et al employed this synthetic tool for the synthesis of various terpenoids, e.g., di-dihydrocarvone (79), 4-methyl-isopropenyl cyclohexane (80) and ar-\(\alpha\)-curcumene (81). The scheme depicting the synthesis of ar-\(\alpha\)-curcumene is
In the present dissertation Wittig reaction has been employed in the syntheses of monocyclic monoterpenes, \( \Delta \)-terpineol; acyclic monoterpenes, geraniolene; and monocyclic aromatic sesquiterpenoid dehydro-\( \alpha \)-curcumene. These are placed in the Chapters I, IV and II respectively. Further employing the Wittig and modified Wittig reactions on suitable compounds with carbonyl functions, the synthesis of \((\pm)\) lanceol has been achieved which is mentioned in Chapter III. Synthesis of dl-carvestrene has been achieved by the application of hydrogenolysis reaction with sodium and ethanol in liquid ammonia on the suitably constituted allylic alcohol. This is included in Chapter V. Syntheses of 1(7),4(8)-\( \psi \)-menthadiene and \( \gamma \)-terpineol have been accomplished by the application of both modified Wittig and hydrogenolysis reactions. These are

\[ \text{Ar} - \underline{\text{\( \gamma \)-CURCUMENE}} \]
recorded in the Chapters VI and VII respectively.

Chapter VIII contains a sesquiterpenoid pyran ether known as curcumene ether which has been obtained by the dehydration of suitably constituted diol.

Dl-ar-turmerone obtained by the grignard reaction of a suitably placed carbonyl function and subsequent oxidation is presented in Chapter IX.