CHAPTER - I.1

GENERAL INTRODUCTION

In the past few decades, organic chemistry has witnessed a tremendous growth in the development of newer methodologies for the synthesis of wide variety of valuable synthetic products. The clear success in the synthesis of the desired product involves the proper designing of the experimental approach having convenient and simple procedure, and the best possible selection of the appropriate organic substrates, specifically needed for such synthesis.

A powerful addition to this aspect is the discovery of numerous selective reagents which owing to their versatile applicability and utility have played an important role in the development and understanding of synthetic organic chemistry. The majority of the reagents which fall in this category are recently discovered sulfonyl halides, mercuric salts, nitrosyl chloride, nitryl iodide, different carbene and carbenoid species etc.

These reagents undergo wide variety of reactions with different organic substrates. The most familiar among such reactions are the addition reactions with a variety of olefinic compounds. These reagents readily add on to the double bond of olefins to afford wide variety of useful addition products.
The course of such addition reactions is governed by the orientation of the double bond in the substrate and a stereospecific, stereoselective or rearranged product may be formed. Besides the nature of the double bond, various other factors such as steric and electronic effects, the nature of the reagent, i.e., electrophilic and/or nucleophilic, its attacking strength, nature of the neighbouring group, reaction medium and temperature also influence the stereochemistry and course of addition reaction.

It has been observed that the addition of electrophilic reagents, such as chlorine, bromine, sulfinyl halides, mercuric salts and protic acids to simple cyclic and acyclic olefins usually occur with the trans-stereochemistry (scheme -1). In highly stereospecific trans additions, a three membered olefin electrophile ring complex (1) is formed and an addition product is obtained with inverted configuration (SN-2-Markovnikov addition) as illustrated in scheme 2.

The additions of electrophilic reagents like hypochlorous acid, bromine and sulfinyl halides to the strained bicyclic olefins e.g., norbornene (2) furnish trans addition products as well as rearranged products (scheme -3), while additions of electrophiles such as mercuric salts, nitrosyl chloride, protic acids with bicyclic olefins does not undergo trans addition but gives a rearranged or cis addition product (scheme -4).
SCHEME 1

\[
\text{R}_\text{C} = \text{C} + \text{E}^+ \text{Y}^- \xrightarrow{} \text{R}_\text{C} = \text{C}
\]

SCHEME 2

\[
\text{R}_\text{C} = \text{C} + \text{E}^+ \xrightarrow{\text{Y}^-} \text{R}_\text{C} = \text{C}
\]  

(1)

SCHEME 3

(2)  

\[
\text{R}_\text{C} = \text{C} + \text{E}^+ \text{Y}^- \xrightarrow{} \text{R}_\text{C} = \text{C}
\]

(3)  

(4)

SCHEME 4

\[
\text{R}_\text{C} = \text{C} + \text{NOCl} \xrightarrow{} \text{R}_\text{C} = \text{C}
\]  

Rearranged product
Exhaustive work has been done on the synthetic utility of various electrophilic and nucleophilic addition reactions across carbon-carbon double bond using a number of reagents which cover numerous publications on the different aspects of the subject. It is beyond the limit of this chapter to cover the diverse aspects of addition reactions with vast number of reagents employed for this purpose. However, literature survey on the chemistry of carbene and nitryl iodide additions to carbon-carbon double bond has been made as work on addition of these reagents to terpenoidal hydrocarbons has been described in this thesis subsequently.

Carbene Addition and Insertion Reactions

The addition of methylene biradicals or carbones have gained recent attention due to their importance in the synthesis of cyclopropanes. Carbones are electrically neutral organic species which contain, at least in one of their valence bond representations, a divalent carbon atom associated with only six valence electrons. Four of these valence electrons are involved in the two covalent bonds, leaving two nonbonding electrons which may be paired with spins opposed in one of the two available orbitals of the central carbon atom (singlet state) or may occupy separate orbitals, usually with parallel spins (triplet state).

Methylene transfer reactions proceed in two steps, (i) dissociation of the methylene donor to produce a carbene,
and (ii) reaction of the carbene with the methylene acceptor (scheme -5).

The other mechanism involves a bimolecular reaction between methylene donor and methylene acceptor which leads to a concerted displacement of the groups A, B by the groups Y, Z (scheme - 6).

The addition of carbenes to olefins furnished stereospecific as well as stereoselective addition products depending upon the orientation of the double bond, e.g., olefins lacking symmetry axis along the carbon-carbon double bond such as 2-butene, can form two adducts with a symmetrical carbene (scheme -7).

In stereospecific cis additions, the geometry of the substituent groups is retained i.e., cis-1,2-dialkyl-cyclopropanes are produced from cis olefins, and trans-1,2-dialkyl-cyclopropanes are obtained from trans-olefins.

In a nonstereospecific reaction, the arrangement of substituents relative to the plane of the ring does not correspond to the configuration of the olefin and addition yields identical product mixtures from cis, trans pairs of alkenes. If different product distributions are observed, the reaction exhibits some degree of stereospecificity. Two major causes of non-stereospecific formation of cyclopropanes can be assigned. (i) initial stereospecific addition, followed by geometrical isomerization of the products, and (ii) non-stereospecific
**SCHEME 5**

\[ R_2C \rightarrow A-B + R_2C: \quad Y-Z \rightarrow R_2C \]

**SCHEME 6**

\[ A-B-C-Y-Z \]

**SCHEME 7**

\[ \text{stereo specific} \]

\[ \text{nonstereo specific} \]

\[ (\text{cis}) \quad (\text{trans}) \]

\[ R_2C + Y-Z \rightarrow R_2C + A-B \]
addition, proceeding through an intermediate whose geometry is less rigid than that of ground state olefins and cyclopropanes.

The reaction of a monosubstituted carbene with olefins, lacking both a centre of symmetry and a two-fold symmetry axis along the carbon-carbon double bond e.g., cis-2-butene, is highly stereospecific and two different adducts are obtained. The isomeric products are designated as syn/anti or endo/exo pairs, the syn or endo configuration being assigned to the cyclopropane in which the carbene substituent has a cis relationship to the larger number of alkyl groups. This nomenclature may also be assigned to the adducts from disubstituted, unsymmetrical carbenes by adding the group to which the syn/anti definition applies (scheme-8).

The two adjacent groups attached to the divalent carbene carbon may be replaced or substituted by a number of organic and inorganic groups to give mono- and disubstituted carbenes such as halocarbenes, dihalocarbenes, phosphoryl carbenes, sulfenyl carbenes, vinyl carbenes, aryl carbenes, cyanocarbenes, ketocarbenes etc.

**Generation of Carbenes: the methods and their scope and mechanism**

The methylene, dihalocarbenes and other carbenoids are highly reactive, unstable and transient species which cannot be isolated in free state and hence their generation is possible only in solution in presence of the substrate with which it has
to react 'in situ'. There are, however, a number of methods available in the literature for the generation of carbenes and carbenoids which are of great significance from the point of view of the theoretical and practical understanding of the carbene chemistry.

(i) **Diazooalkanes and related compounds**

Diazooalkanes are widely used as source of carbenes and carbenoids due to their tendency to lose a molecule of nitrogen on heating or irradiation. These compounds are prepared from a stable precursor, such as an alkali metal salt of the toluene-p-sulfonyl-hydrazone (tosyl hydrazone) of the corresponding carbonyl compounds in the appropriate solvent and decomposed 'in situ'. (Bamford-Stevens reaction, scheme 9).

In protic solvents such as alcohol, diazooalkanes react with loss of nitrogen either involving carbene\(^8,9,10\) or carbonium\(^11\) ion intermediate and so the position of diazooalkyl diazonium ion equilibrium is important in determining the course of reaction\(^12,13\). Thus the proportions of products in Bamford-Stevens reactions show a dependence on the base concentration used (scheme-10).

The reaction of camphor tosyl hydrazone (5) with sodium methoxide in diglyme furnishes tricyclene (6) an intramolecular insertion product of the carbene derived from diazocamphor and camphene (7), derived from the corresponding carbonium ion since its formation is favoured in protic solvents of high protonating ability. However the ratio of camphene to tricycl
**Scheme 8**

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

\[ + :\text{CHR} \rightarrow \]

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

(syn or endo) (anti or exo)

**Scheme 9**

\[
\begin{align*}
\text{C} & \quad \text{N} \quad \text{NHSO}_2 \\
\text{R} & \quad \text{R'} \\
\text{C} & \quad \text{H}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{C} & \quad \text{N} \quad \text{NHSO}_2 \\
\text{R} & \quad \text{R'} \\
\text{C} & \quad \text{H}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{R} & \quad \text{R'} \\
\text{C} & \quad \text{N}_2 \\
\text{C} & \quad \text{H}_3 \\
\end{align*}
\]

Fast

\[
\begin{align*}
\text{R} & \quad \text{R'} \\
\text{C} & \quad \text{N}_2 \\
\text{C} & \quad \text{H}_3 \\
\end{align*}
\]

Slow

\[
\begin{align*}
\text{R} & \quad \text{R'} \\
\text{C} & \quad \text{N}_2 \\
\text{C} & \quad \text{H}_3 \\
\end{align*}
\]

**Scheme 10**

\[
\begin{align*}
\text{R} & \quad \text{R'} \\
\text{C} & \quad \text{CNN} \\
\text{H} & \quad \text{X} \\
\end{align*}
\]

\[
\begin{align*}
\text{R} & \quad \text{R'} \\
\text{C} & \quad \text{CNN} \\
\text{H} & \quad \text{X} \\
\end{align*}
\]

\[
\begin{align*}
\text{R} & \quad \text{R'} \\
\text{C} & \quad \text{CNN} \\
\text{H} & \quad \text{X} \\
\end{align*}
\]

\[
\begin{align*}
\text{R} & \quad \text{R'} \\
\text{C} & \quad \text{CNN} \\
\text{H} & \quad \text{X} \\
\end{align*}
\]

\[
\begin{align*}
\text{R} & \quad \text{R'} \\
\text{C} & \quad \text{CNN} \\
\text{H} & \quad \text{X} \\
\end{align*}
\]
decreases with increasing base concentration, and, when, deuterium oxide is present, the tricyclene produced contains deuterium in an amount which also decreases as the sodium methoxide concentration goes up\(^{14}\)(scheme -11).

Carbene formation is the principle reaction path in the thermal decomposition of diazoalkanes in protic solvents e.g., decomposition of phenyl and diphenyl diazomethane in acetonitrile which indicates a primary unimolecular process\(^{15,16}\). In reaction of olefin and diazomethane, cyclopropanes are obtained either through the formation of carbene or pyrazoline by 1,3-dipolar cycloaddition depending upon the concentration of olefin (scheme -12).

In contrast to the thermal decomposition in which carbenes are produced from the ground state of a diazoalkane be initially in the singlet state, photolysis of diazo compounds yield directly either triplet or singlet carbene depending on wheather or not a triplet photosensitizer [e.g., Hg\(^{3}P\) atoms, benzophenone] is used. In certain reactions, diazomethane is known to act as a photosensitizer\(^{18}\).

Diazooalkanes undergo decomposition in the presence of number of metallic derivatives\(^{10,19}\) such as metal halides of mercury, zinc and cadmium and Lewis acids e.g. boron compounds and lead to the formation of \(\alpha\)-haloalkyl metal halides which are isolated in some cases\(^{20}\) and show carbenoid reactivity (scheme -13).
SCHEME 11

(5) \[ \overset{\Delta}{\longrightarrow} \]
\[ \overset{\text{RO}^+}{\leftrightarrow} \]
\[ \overset{\text{RO}^-}{\rightarrow} \]

\[ \text{N-N} \]
\[ \text{H} \]

\[ \text{H} \]

\[ \text{H} \]

\[ \text{H} \]

\[ \text{H} \]

\[ \overset{\text{Insertion}}{\rightarrow} \]
\[ \overset{-\text{H}^+}{\rightarrow} \]
\[ \overset{(i) \ 1,2-\text{shift}}{\rightarrow} \]
\[ \overset{(ii) \ -\text{H}}{\rightarrow} \]

(6)

(7)

SCHEME 12

RR'C:

RR'CNN

\[ \overset{-\text{N}_2}{\text{slow}} \]

\[ \overset{\text{fast}}{\rightarrow} \]

\[ \overset{\text{fast}}{\rightarrow} \]

\[ \overset{-\text{N}_2}{\text{slow}} \]
The decomposition of diazoalkanes induced by metallic copper and copper derivatives, in the presence of olefins, furnish cyclopropanes through the electrophilic intermediate complexes of the type \( \text{RR'}C^+\text{MX}_n^- \), in contrast to free carbene generated by photolysis. Thus the carbenoid involved shows little tendency to insert into C-H bonds and its stereoselectivity in cyclopropane formation from olefins differs from that of the corresponding carbene. Nozaki et al. observed that the chiral copper complex (8) induces optical activity in the mixture of the cyclopropanes produced from styrene and ethyl diazoacetate (scheme-14). The steric course of such carbenoid additions depend upon the size and electronic nature of ligand attached to copper \( ^24(A) \).

The formation and reaction mechanisms of methylene derivatives from diazo compounds has recently been reviewed. \( ^24(B) \)

(ii) Base induced-\( \alpha \)-elimination

The base induced-\( \alpha \)-elimination reaction requires a basic reagent MB e.g., potassium tert-butoxide or lithium butyl to generate a carbanion (or its organometallic reagent) from the substrate e.g., an organic halide or gem-dihalide and loss of \( M^+ X^- \) then gives the carbene (scheme-15). Carbene formation by this type of mechanism was first conclusively demonstrated by Hine \( ^{25} \) in the hydrolysis of chloroform to carbon mono-oxide and formate ion.
**SCHEME 13**

$$RR'C \cdot NN \xrightarrow{MXn} \left[ RR'\left( N_2^+ \right) MXn \right] \xrightarrow{-N_2} RR'C(X)MX_{n-1}$$

**SCHEME 14**

$$\text{C}_{6}H_{5}-\text{CH-CH}_{3}+\text{Cu}-\text{N} \rightarrow \text{Ph} \cdot \text{H} \cdot \text{Ph} \cdot \text{COOEt}$$

**SCHEME 15**

$$RR'CHX \xrightarrow{MB} RR'C X^- M^+ \xrightarrow{-M^+ X^-} RR'C : \xrightarrow{Products}$$
Doering and Hoffmann\textsuperscript{26} were first to carry out the successful application of this technique by the addition of dihalocarbenes to olefins in the presence of potassium tert-butoxide and isolated cyclopropanes in good yields. In place of potassium tert-butoxide, sodium methoxide\textsuperscript{27-29}, potassium isopropoxide\textsuperscript{30} and a dispersion of sodium hydroxide\textsuperscript{31} may also be used.

The application of two phase catalytic systems in the chemistry of polyhalomethyl carbanions and halocarbenes is particularly important and has attracted significant attention. In 1969, Makosza et al.\textsuperscript{32(A)} reported that in the presence of concentrated aqueous sodium hydroxide and triethyl benzyl ammonium chloride (TEBA) catalyst, chloroform is readily converted into trichloromethyl anion and then dichlorocarbene which in turn can be effectively trapped with alkenes giving corresponding dichlorocyclopropane derivatives in high yield.

An ameloored technique of phase-transfer catalysis given as above, was reported by Julia and Ginobreda in 1977\textsuperscript{32(B)} Dihalocarbenes were generated by using solid-liquid phase transfer catalysis involving the action of powdered sodium hydroxide, haloform and phase transfer catalysts. Tetraethyl ammonium fluoride in acetonitrile also gives $\alpha$-eliminations of hydrogen halides from haloforms\textsuperscript{33}.

Dihalocarbene adducts were also prepared by heating equimolar amounts of haloform and olefin in presence of ethylene oxide and catalytic amounts of tetraethylammonium bromide.
at elevated temperatures (130-170°) and high pressure\textsuperscript{34,35}. Tri and tetraalkyl-1,1-dihalocyclopropanes undergo rearrangement and dehydrohalogenation under these reaction conditions, with formation of halo-1,3-dienes\textsuperscript{36}.

(iii) Organometallic reagents

Simmons and Smith\textsuperscript{37} were the first to investigate the stereospecific synthesis of cyclopropanes by treatment of olefins with methylene iodide and zinc copper couple in good yields. The addition is exclusively \textit{cis} and the reaction rate is proportional to the olefin concentration (scheme-16). Methylene transfer occurs via the transition state (9)\textsuperscript{38}.

Sawada and Inouye\textsuperscript{39} modified the Simmons and Smith reaction\textsuperscript{37} in order to achieve improved yields of cyclopropane adducts from various olefinic substrates. The method involves a prior reaction of ethyl iodide with zinc copper couple followed by addition of methylene iodide and olefin.

Nishimura et al\textsuperscript{40} synthesized cyclopropane products from cationically polymerizable olefins such as vinyl ethers by its treatment with dialkyl zinc and methylene iodide. A stereospecific reaction of olefins with ethylidene iodide and diethyl zinc furnished methyl cyclopropanes in improved yields\textsuperscript{41}.

Seyferth and coworkers\textsuperscript{42-55} have demonstrated the outstanding utility of halomethyl mercury compounds as methylene transfer agents. Using the appropriate mercurials, various
divalent carbon species may be added to the olefinic double bonds or inserted into the α-C-H bonds of allyl ethers and into the Si-H bonds of alkyl silanes.

The methylene transfer reactions of trihalomethyl phenyl-mercury (PhHgCX₃) do not involve radicals or trihalomethide ions. Acetonitrile, acrylic acid esters, vinyl acetate, styrene and butadiene are not polymerized during their reactions with phenyl (bromodichloromethyl) mercury. Thus, the reaction of vinyl acetate with PhHgCl₂Br furnishes dihalocarbene adduct (10) as the sole product in 80 percent yield while the reaction of Cl₂C⁻, generated by the decarboxylation of sodium trichloroacetate, with vinyl acetate gives both 2,2-dichlorocyclopropyl acetate (10) and the addition product, 1-trichloromethylthyl acetate (11) in comparable yields (scheme 17).

The action of sodium iodide in acetone or dimethoxyethane on phenyl (trihalomethyl) mercury compounds results in displacement of trihalomethyl anions from mercury with formation of PhHgI. This reaction proceeds faster than the thermal decomposition of PhHgCX₃. In acetone, the X₂C⁻ species is intercepted by protonation or addition to the solvent; in dimethoxyethane, good yields of cyclopropanes are obtained with the more reactive olefins. BrCl₂C⁻ is partitioned to give minor amounts of gem-chlorobromocyclopropanes along with gem dichlorocyclopropanes as the major products. In contrast, the thermolysis of PhHgCl₂Br produces dichlorocyclopropanes only (scheme 18).
Difluoromethylene can be generated in a similar manner by the action of sodium iodide on the organo-tin compound \((\text{CH}_3)_2\text{SnCl}_3\)\(^{57,59}\), whereas organosilicon halides such as \(\text{Cl}_3\text{SiCOCl}_3\) decompose unimolecularly to give silicon tetra-chloride and the carbene directly\(^{60}\).

Carbene generation by the thermal decomposition of a sulfene through a three step mechanism was reported as early as 1911 by Weckkind\(^{61}\) to account for the formation of stilbene from phenylmethanesulfonyl chloride and triethyl amine. However, the three step mechanism for the decomposition of sulfene was contradicted by King et.al\(^{62}\) and it has been shown that the reaction proceeds via a two step mechanism.
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CHAPTER I.2

Addition of dichlorocarbene to terpenoidal olefins

ABSTRACT

The reaction of sesquiterpenoidal olefins such as longifolene and isolongifolene with dichlorocarbene generated by the procedure of liquid-liquid phase transfer catalysis, was carried out. Longifolene gave \textit{endo}-longibornyl-7-spiro-1'-(2',2'-dichlorocyclo-propane) whereas isolongifolene furnished a diastereomeric product in 1:1 ratio. Further, the reaction of monoterpenoidal olefins such as terpinolene and \(\gamma\)-terpinene having environmentally different two carbon-carbon double bonds with dichlorocarbene generated by the method of solid liquid phase transfer catalysis was done. Terpinolene gave \textit{trans}-1-methyl-7,7-dichloronorcaran-4-spiro-(1',1'-dimethyl-2',2'-dichlorocyclopropane) whereas \(\gamma\)-terpinene yielded \textit{trans}-4,4,8,8-tetrachloro-1-methyl-5-isopropyl tricyclo[5.1.1.0]octane. It was observed that both the dienes gave the diadducts as the major product of the reaction.
INTRODUCTION

The chemistry of addition reactions of carbenes and carbenoids with wide variety of cyclic and acyclic olefins has been extensively investigated and reviewed\(^1\). However, comparatively smaller amount of work on the addition reactions of carbenes with terpenoidal olefins has been done so far. The study of carbene addition reactions with terpenoidal olefins is of great significance from the viewpoint of its versatile applicability and utility in the synthesis of terpenoidal cyclopropane compounds and for the understanding of mechanistic mode of carbene/carbenoid addition of terpenoidal olefins, along with the determination of selectivity of the reaction on the double bond towards various carbene and carbenoid species.

The first important paper in this field was published by Doering and Hoffmann\(^2\). They found that the reaction of \(\beta\)-pinene(1) with dibromocarbene, generated 'in situ' by the dehydrobromination of bromoform with potassium tert-butoxide in cyclohexane, affords an addition product (2). However, \(\alpha\)-pinene (3) failed to undergo such transformation under similar reaction conditions (scheme - 1). This paper signaled the beginning of a new era in the synthesis of terpenoidal cyclopropanes by carbene addition to the carbon-carbon double bond of terpenoidal hydrocarbons.
It has been observed that the reaction of (+) and (-) \(\alpha\)-pinene\(^3\) (3A,3B) with dichlorocarbene, generated 'in situ' by the action of potassium tert-butoxide with chloroform in n-hexane at \(-10^\circ\) furnished trans (+) and (-) 2,8,8-trimethyl-3,3-dichlorocyclo[4.1.1.0] octane (4A, B)(scheme - 2), respectively. The trans-pinene ring conformation was assigned on the basis of high steric interaction between gem-dichloro group (at C\(_3\)) and gem-dimethyl (at C\(_8\)) in cis conformation. The steric hinderence in trans conformation seems to have been minimized as the gem-dichloro group is far apart from the gem dimethyl group of the bridge as illustrated in scheme 2.

However, the reaction of (+)-\(\alpha\)-pinene (3A) with dibromocarbene under similar reaction conditions afforded a different type of rearranged olefinic product, 2,8,8-trimethyl-3-bromobicyclo[4.1.1] oct-2-ene (5)(scheme - 2) and not the expected gem dibromocyclopropyl adduct (6). The rearranged olefinic product(5) appears to have been formed as a result of dehydrobromination of gem-dibromocyclopropyl adduct (6).

In contrast to the observations of Doering et.al\(^2\), Muhlstaedt et.al\(^4\) successfully isolated the gem-dibromocyclopropyl adduct resulting from the reaction of \(\alpha\)-pinene(3) with dibromocarbene at \(10^\circ\). The gem-dibromocyclopropyl adduct was identified to be 3,3-dibromo-2,8,8-trimethyl tricyclo[4.1.1.0] octane(6) by subsequent reduction with sodium in liquid ammonia to furnish (+)-2,8,8-trimethyl tricyclo [4.1.1.0]
**SCHEME 1**

\[
\begin{align*}
(1) & \xrightarrow{\text{CBr}_2} (2) \\
(3) &
\end{align*}
\]

**SCHEME 2**

\[
\begin{align*}
(3) & \equiv \\
(4) & A = (+) - \text{pinene} \\
& B = (-) - \text{pinene} \\
(3A) & \xrightarrow{\text{CBr}_2} (6) \\
(5) &
\end{align*}
\]
octane (7)(scheme – 3). The adduct (6) is less stable at room temperature and transforms into (+)-2,3-dibromo-2,8,8-trimethyl bicyclo[4.1.1] oct-3-ene (8). When this adduct (6) was subjected to distillation under reduced pressure, a brown liquid was obtained which after chromatographic purification was shown to be (+) 3-bromo-2-methylene-8,8-dimethyl bicyclo[4.1.1] oct-3-ene (10) as evidenced by IR, UV and high resolution NMR spectral analysis.

The instability of product (6) is attributed to the tension in tricyclo[4.1.1.0] octane group and to the strong non-bonding exchange interaction between the substituents. Both the factors affecting the stability of the product (6) can be minimized when the molecule reacts like a cyclopropyl allyl complex. This complex obeys the principle of conservation of orbital symmetry5. Therefore adduct (6) undergoes electrocyclic transformation and according to the principle of least motion6,7 forms product (8) and 2,8,8-trimethyl bicyclo[4.1.1] oct-2-ene (9). The splitting of HBr leads to the formation of (10) and 3-bromo-2,8,8-trimethyl bicyclo[4.1.1] octa-2,4-diene (11) as illustrated in scheme – 4.

The reaction of α-pinene (3) with dichlorocarbene generated by an alternative procedure8 which involves the action of sodium methoxide with ethyl trichloroacetate gave an endo addition product (4) in 97 percent yield. The product (4) was also obtained by using solid-liquid phase transfer
catalysts like benzyl triethyl ammonium chloride and powdered sodium hydroxide, for generation of dichlorocarbene.

Interesting observations on the reactions of dichlorocarbene with \( \beta \)-pinene (1) and other terpenoidal olefins have been recorded by Muhlstaedt et al. \(^9\). Thus \( \beta \)-pinene (3) reacted smoothly with dichloro- and dibromocarbene, in an identical manner, to afford \((+)-7,7\text{-dimethyl-norpinane-2-spiro-1'-}[2',2'\text{-dichlorocyclopropane}] \) (12) and \((+)-7,7\text{-dimethyl norpinane-2-spiro-1'-}[2',2'\text{-dibromo cyclopropane}] \) (13) respectively in high yields. The compounds (12) and (13) on reduction with sodium in liquid ammonia furnished dehalogenated product, 7,7\text{-dimethyl norpinane-2-spiro-1'-cyclopropane} (14) (scheme - 5).

It has also been reported \(^9\) that the reaction of \((+)-\)camphene (15) with dichlorocarbene, generated by the procedure outlined by Parham and Schweizer \(^{10}\) using ethyl trichloroacetate and sodium methoxide at \(-10^\circ\)C, gave an addition product in 72 percent yield. The product was characterized to be \((+)-2,2\text{-dimethyl norbornan-3-spiro-1'-}[2',2'\text{-dichlorocyclopropane}] \) (16) by spectral analysis (scheme - 6).

In an analogous reaction of Camphene (15) with dibromocarbene, generated by the procedure of Doering et al. \(^2\), \((+)-2,2\text{-dimethyl norbornan-3-spiro-1'-}[2',2'\text{-dibromocyclopropane}] \) (17) (scheme - 6) was obtained in 78 percent yield. The same product (17) was also obtained by Saxena and Bokadia \(^3\), comparatively in lower yields. The dichloro- and dibromo adducts (16)
and (17) on reduction with sodamide gave the dehalogenated product (+)-2,2-dimethyl norbornane-3-spiro-1'-cyclopropane (18) (scheme - 6), in 70 - 80 percent yield.

The reaction of dichlorocarbene with (-) sabinene\(^9\) (19) gave (-)-1-isopropyl bicyclo [3.1.0] hexan-4-spiro-1'-[2',2'-dichloro-cyclopropane] (20) in 75 percent yield while its reaction with dibromocarbene afforded (-)-1-isopropyl bicyclo [3.1.0] hexan-4-spiro-1'-[2',2'-dibromo-cyclopropane] (21) in fair yields. The structures of (20) and (21) were confirmed by their subsequent reduction with sodamide to give dehalogenated product (-)-1-isopropyl bicyclo [3.1.0] hexan-4-spiro-1'-cyclopropane (22) (scheme - 7).

The reaction of \(\Delta^3\)-carene (23) with carbene generated by the action of methylene chloride and n-butyl lithium at -40°C gave an isomeric mixture\(^11\) in the ratio 40:60. The two isomers were separated by preparative gas chromatography and identified to be syn, trans-8-chloro-1,4,4-trimethyl tricyclo [5.1.1.0] octane (26) and anti, trans-8-chloro-1,4,4-trimethyl tricyclo [5.1.1.0] octane (27) respectively. Reduction of (26) and (27) with sodium in liquid ammonia furnished 1,4,4-trimethyl tricyclo [5.1.1.0] octane (25) (scheme - 8).

Further it was found\(^15\) that the reaction of \(\Delta^3\)-carene (23) with dibromocarbene, generated 'in situ' by potassium tert-butoxide and bromoform in cyclohexane at -10°C gave trans-8,8-
SCHEME 7

(19) \[ \text{or/and} \]

(20) \( R = \text{Cl} \)
(21) \( R = \text{Br} \)

(22)

SCHEME 8

(23) \[ \text{Redn} \]

(24) \[ \text{Redn} \]

(25)

(26)

(27)
dibromo-1,4,4-trimethyl tricycle [5.1.1.0] octane (28) exclusively\textsuperscript{12,15}. Reduction of the product (28) furnished anti, \textit{trans}-8-bromo-1,4,4-trimethyl tricycle [5.1.0.0] octane (29) and syn, \textit{trans}-8-bromo-1,4,4-trimethyl tricycle [5.1.0.0] octane (30), each isomer existing in two conformations with a nearly flat six membered ring as concluded by NMR spectra (scheme - 9).

The reaction of chlorocarbene with $\Delta^3$-carene\textsuperscript{16} (23) gave the products (26) and (27) which on reduction with sodium in liquid ammonia gave (25) similar to the products obtained by Erdtman and Westfelt\textsuperscript{11}. Further the reaction of $\Delta^3$-carene (23) with dichlorocarbene, generated by ethyl trichloro-acetate and sodium methoxide in n-hexane gave a product of molecular formula $C_{11}H_{16}Cl_2$ in 70 percent yield, which on reduction with sodium the liquid ammonia gave (25). The isolation of (25) proved the structure of the product obtained by the addition of dichlorocarbene to be \textit{trans}-1,4,4-trimethyl tricycle[5.1.1.0] octane (24) (scheme - 8).

The reaction of $\Delta^3$-carene(23) with carbene dichloro- and dibromocarbene\textsuperscript{17} using methylene iodide and zinc copper couple in dry ether to give carbene adduct; ethyl trichloroacetate in heptane to obtain dichloro-carbene adduct and potassium tertiary butoxide, bromoform in petroleum ether to furnish the dibromocarbene adduct in 35.7, 28 and 29 percent yield respectively.
Orthodene (32) on reaction with dichloro-carbene generated by the method of Parham et al., affords 3,3-dichloro-4,7,7-trimethyl tricyclo [4.1.1.0] octane (33) with trans stereochemistry as evidenced by its NMR spectra. Reduction of (33) with n-ethyl morpholine in presence of lithium aluminium hydride at 115°C gave an isomeric mixture of 4-chloro-3,7,7-trimethyl bicyclo [4.1.1] oct-3-ene (34) and 4-chloro-3,7,7-trimethyl bicyclo [4.1.1] oct-4-ene (35) in 73 percent and 10 percent yields respectively (scheme - 10). Similar reaction of dichlorocarbene with apopinene (36) gave 3,3-dichloro-7,7-dimethyl tricyclo [4.1.1.0] octane (37) in 35 percent yield. The product (37) undergoes reduction to give a terpenic hydrocarbon, 7,7-dimethyl tricyclo [4.1.1.0] octane (38) (scheme - 11).

The addition of dichlorocarbene to trans-6-pinene (39) at -15°C and 5°C did not give an adduct and unreacted olefin was recovered as such from the reaction mixture. Attempts to isolate the addition product by the reaction of trans-6-pinene (39) and dichlorocarbene generated by the thermal decomposition of trichlorophenyl methyl mercury at 80°C in benzene also proved unsuccessful.

The reason for the failure to isolate an adduct of dichlorocarbene with trans-6-pinene (39) is attributed to the steric hindrance of C-10 methyl group, which owing to its
**SCHEME 9**

(23) $\xrightarrow{CBr_2} (28) \xrightarrow{\text{Redn.}} (31)$

(29) $\xrightarrow{\text{Redn.}}$ $\xrightarrow{H} (30)$

**SCHEME 10**

(32) $\xrightarrow{CCl_2} (33) \xrightarrow{\text{Redn.}} (34) + (35)$

**SCHEME 11**

(36) $\xrightarrow{CCl_2} (37) \xrightarrow{\text{Na/NH}_3} (38)$
trans configuration prevents the attack of dichlorocarbene on the carbon-carbon double bond.

In contrast to the above observations, dichlorocarbene under similar circumstances readily adds to the double bond of \( \text{cis-8-pinene} \) \(^8\) (40) to furnish \( \text{trans-2-dichloro-methyl-2,6,6-trimethyl bicyclo [3.1.1] hept-3-ene} \) (41) (scheme - 12) in excellent yield of 71 percent.

The reaction of myrcene \(^{20}\) (42) with dichlorocarbene, carbethoxy carbene and methylene has been done with a view to explore the selectivity and specificity of carbene additions on the susceptibility of three environmentally different double bonds present in myrcene (42). The reaction of myrcene (42) with dichloro-carbene, generated from chloroform using two phase system, aqueous sodium hydroxide (50 percent), chloroform with catalytic amount of TEBA \(^{21,22}\) gave (43) as a major product in 42 percent yield (scheme-13). The structure of (43) was ascertained by NMR and mass spectroscopy. It follows that the electrophilic character of dichlorocarbene results in a preferential addition to the more substituted double bond. Since (43) has two chiral atoms, hence it exists in two diastereomeric forms. The NMR spectral analysis also indicates that both isomers are present in equal amounts.

The reaction of myrcene with carbethoxy carbene was reported as early as 1924 by Staudinger, Ruzicka and coworkers \(^{23}\)(A), but the structure of the reaction product
could not be ascertained. De-Smet et al.\textsuperscript{20} successfully isolated the reaction products (44) and (45) on reaction of myrcene (42) with carbethoxy-carbene generated by the thermolysis of ethyl diazoacetate in presence of copper sulphate\textsuperscript{23(B)} (scheme - 14). The possible \textit{cis}/\textit{trans} isomeric formulation of the above two products has been represented by structures (44A), (44B) and (45A), (45B). It was observed that the variations in the experimental conditions controlled the regiospecificity of the reaction to a great extent. From the products thus obtained by the reaction of carbethoxycarbene with myrcene, it has been shown that carbethoxy-carbene preferentially attacks at the least substituted double bond from the least hindered side.

The reaction of myrcene (42) with methylene generated by Simmons and Smith\textsuperscript{24} procedure following an ameliorated technique\textsuperscript{25,26} was a concerted one and gave a product containing mono, di-, and tri-adducts which in turn depends on the varying reactant ratios used at the time of commencement of the reaction. Thus (1:1) ratio of myrcene and methylene furnished products formulated as (46) and (47) (scheme 15).

The reaction of limonene\textsuperscript{27}(48) with dichlorocarbene generated by using liquid-liquid phase transfer catalysts gave the diadduct (49) in 72 percent yield (scheme 16). The product (49) seems to have been formed by the insertion of two moieties of dichlorocarbenes at both the carbon-carbon double bonds of the hydrocarbon. The product (49) was also obtained
obtained in an yield of 68 percent by the reaction of limonene with dichlorocarbene generated by a new technique viz., solid-liquid phase transfer catalysis.

Similarly the reaction of dichlorocarbene with trans-isolimonene (50), isomeric to limonene, has been reported to furnish 98.2 percent of diastereomeric products (51) and (52) in equal ratio and 1.8 percent diastereomeric products (53) and (54)(scheme-17). It is quite apparent from the above reaction that in the case of trans-isolimonene, although it contains two carbon-carbon double bonds creating two reactive sites for the attack of carbene species only monoaducts are formed exclusively in all the four diastereomeric products. However in the case of limonene diadducts are formed due to the simultaneous attack of carbene moieties over both the carbon-carbon double bonds.

In the light of work done till now on the addition reactions of carbenes and carbenoids, using different carbenoid precursors to the carbon-carbon double bonds of terpenoidal hydrocarbons, it was considered worthwhile to extend the work to some more terpenoidal olefins with a view to investigate the reactivity and selectivity of the carbenes towards the addition to the double bonds, and to study the mode of addition and stereochemistry of the products thus obtained. Among various carbone species, dichlorocarbene was selected for the purpose and its reaction with sesquiterpene hydrocarbons,
SCHEME 15

(42) \xrightarrow{\text{CH}_2} \begin{array}{c}
\begin{array}{c}
(46) \\
+ \\
(47)
\end{array}
\end{array}

SCHEME 16

(48) \xrightarrow{\text{CCl}_2} \begin{array}{c}
\begin{array}{c}
(49) \\
\end{array}
\end{array}

SCHEME 17

(50) \xrightarrow{\text{CCl}_2} \begin{array}{c}
\begin{array}{c}
(51) \\
+ \\
\text{and} \\
(52) \\
+ \\
(53) \\
+ \\
(54)
\end{array}
\end{array}
longifolene (55), and isolongifolene (57), monoterpene diene terpinolene (59) and γ-terpinene (61) has been carried out.

RESULTS AND DISCUSSION

(i) Addition of dichlorocarbene to longifolene (55)

The reaction of (+)-longifolene (55) with dichlorocarbene, generated 'in situ' from chloroform, aqueous sodium hydroxide (50 percent) and catalytic amount of benzyl triethylammonium chloride, afforded a crude reaction product which was distilled under vacuum to separate the unreacted olefin as identified by the comparison of IR spectrum with that of an authentic sample of longifolene (55).

The residue was chromatographed over silica-gel and elution with benzene-ethyl acetate (9:1) gave the pure reaction product, longibornyl-7-spiro-1'- (2', 2'-dichlorocyclopropane) (56) in an yield* of 50 percent (scheme - 18).

The compound (56) did not decolorise bromine in carbon tetrachloride and gave positive test for chloride. The IR spectrum of longibornyl-7-spiro-1'- (2', 2'-dichlorocyclopropane) (Fig. 1), alongwith other absorption bands, showed characteristic bands at 1060 and 1030 cm⁻¹ indicating the presence of cyclopropane ring. Two bands at 830 and 735 cm⁻¹ are due to

* on the basis of olefin recovered.
the C-Cl stretching vibrations. The NMR spectrum of (56)(Fig. 2) showed signals at δ 0.8 (6H) assigned to gem-dimethyl protons, δ 1.1 (3H) assigned to methyl protons and δ 0.65(2H) assigned to methylene protons attached to the cyclopropane carbon atom. A complex pattern between the range δ 1.25 - 2.1 (13H) is due to the secondary and tertiary protons. However, no signal was observed in the olefinic range. The elemental analysis of (56) agrees with the molecular formula C_{16}H_{24}Cl_{2}.

The compound (56) was found to have an endo stereochemistry (as evidenced by coupling constant, J = 6Hz) and this is in contrast to camphene (15) which gives an exo isomer exclusively on reaction with dichlorocarbene, as reported in the literature^{3}(scheme - 6). It clearly indicates the attack of carbene species to take place from the back side of longifolene, sterically less hindered than the front side (β) which is protected by a large bridge (C_2-C_5) and thus inhibits the addition to occur from this side.

(ii) Addition of dichlorocarbene to isolongifolene (57)

The reaction of dichlorocarbene, generated in a manner similar to that described above, with isolongifolene (57) furnished a crude reaction product. The crude reaction product was distilled under vacuum to recover the unreacted olefin, which was identified by the comparison of its IR spectrum with that of an authentic sample of isolongifolene. The residue was chromatographed over silica-gel and elution with
benzene-ethyl acetate (9:1) gave a diastereomeric product (58) in (1:1) ratio (as evidenced by gas chromatography) in 51 percent yield (scheme 19).

The compound (58) was saturated to bromine in carbon tetrachloride and was found to contain chlorine. The IR spectrum (Fig. 3) showed bands characteristic of C-H bending vibration of cyclopropane at 1030 cm⁻¹ and C-Cl stretching mode at 820, 780 cm⁻¹ besides other absorption bands and no band was found to appear in the olefinic range (1680 - 1620 cm⁻¹). The NMR spectrum (Fig. 4) signalled no peak for olefinic protons and showed a complex absorption pattern for saturated methyl and methylene protons. The elemental analysis is consistent with the molecular formula C₁₆H₂₄Cl₂.

(iii). Addition of dichlorocarbene to terpinolene (59)

The reaction of dichlorocarbene generated by the method of Julia et al.²⁸ using powdered sodium hydroxide, chloroform and a catalytic amount of quaternary ammonium salt, cetyl trimethylammonium bromide, with terpinolene (59) was carried out at room temperature. It was observed that the reaction proceeded fast and was highly exothermic. The reaction mixture was therefore cooled in an ice bath with continuous stirring for one hour to ensure complete reaction. After the usual work up, a crude reaction product was obtained which was distilled under vacuum to remove the unreacted olefin, characterised by the comparison of IR spectrum with that of an
authentic sample. The residue was chromatographed over silica-gel and elution with petroleum ether-benzene (1:1) gave trans-1-methyl-7,7-dichloro-norcaran-4-spiro-(1',1'-dimethyl-2',2'-dichloro-cyclopropane)(60) (scheme 20) in 35 percent yield.

The compound gave positive test for chlorine and was saturated to bromine in carbon tetrachloride. The infrared spectrum (Fig.5) exhibited absorption bands at 1030, 1005 cm⁻¹ characteristic of cyclopropane ring and 820, 760 cm⁻¹ showing the presence of C-Cl linkage.

The NMR spectrum (Fig.5) exhibited peaks at δ 0.92 (3H) assigned to the methyl protons, δ 1.1 (1H) assigned to C₂ tertiary proton (J = 1.0 and 7.8 Hz), δ 1.2 (3H) and δ 1.35 (3H) assigned to gem-dimethyl protons. Multiplets centered at δ 1.54 (4H) were assigned to methylene protons and at δ 1.9 (2H) for secondary protons attached to C₃. No absorption was observed in the olefinic range. The trans configuration of (60) is based on the coupling constant (J = 1.0 and 7.8 Hz). The elemental analysis agrees with the molecular formula C₁₂H₁₆Cl₄.

(iv) Addition of dichlorocarbene to γ-terpinene (61)

The reaction of γ-terpinene (61) with dichlorocarbene generated by the procedure as described above, furnished a crude reaction product which was distilled under vacuum to remove the unreacted olefin, identified by comparison of IR spectrum with that of an authentic sample of γ-terpinene(61).
The residue on repeated crystallizations gave trans-4,4,8,8-tetrachloro-1-methyl-5-isopropyl tricyclo [5.1.1.0] octane (62) (scheme 21) in an yield of 35 percent.

The structural assignment of (62) is based on chemical and spectroscopic analysis. The compound was saturated to bromine in carbon tetrachloride and gave positive test for chlorine.

The infrared spectrum (Fig. 7) of (62) showed bands at 1030, 950 cm\(^{-1}\) indicative of C-H bending vibration of cyclopropane and at 815, 760 cm\(^{-1}\) characteristic of C-Cl stretching vibration mode. No band was found to appear in the olefinic range. The NMR spectrum (Fig. 8) signalled peaks at δ 0.96 (3H) and at 1.08 (3H) assigned to gem-dimethyl protons; δ 1.22 (1H) assigned to the proton at C\(_2\) (J = 1.3 and 7 Hz), δ 1.29 (1H) assigned to the proton at C\(_5\) (J = 1.35 and 6.5 Hz), δ 1.38 (3H) assigned to methyl protons, δ 1.73 (1H) assigned to C\(_8\) proton and a multiplet between δ 2.04 - 2.15 (4H) assigned to the methylene protons. The compound (62) has trans configuration as is evident from the coupling constants. The elemental analysis of the compound is in accordance with the molecular formula \(\text{C}_{12}\text{H}_{16}\text{Cl}_4\).

It seems that both the double bonds of terpinolene (59) and γ-terpinene (61) are simultaneously attacked by the carbene species and it is difficult to determine the reactivity of the two environmentally different double bonds present in
**Scheme 18**

\[ \text{CHCl}_3 + \text{NaOH aq} \rightarrow \text{TEBA} \]

**Scheme 19**

\[ :\text{CCl}_2 \]

**Scheme 20**

\[ :\text{CCl}_2 \]

**Scheme 21**

\[ :\text{CCl}_2 \]
Fig. 1: IR spectrum of endo-longibornylane-7-spiro-1'- (2',2'-dichloro-cyclopropane)(56)
Fig. 2: NMR spectrum of endo-longibornyl-7-spiro-1'-{(2',2'-dichloro-cyclopropane) (56).
Fig. 3: IR spectrum of dichlorocarbone-isolongifolene adduct (90).
Fig. 4: NMR spectrum of dichlorocarbone-isoleucifulone adduct (58).
Fig. 5: IR spectrum of *trans*-1-methyl-7,7-dichloromercarane-4-spiro-(1',1'-dimethyl-2',2'-dichlorocyclopropane) (60).
Fig. 6: NMR spectrum of trans-1-methyl-7,7-dichloronorcarane.
4-spiro-(l',l'-dimethyl-2',2'-dichlorocyclopropane)(60)
Fig. 7: IR spectrum of trans-4,4,8,8-tetrachloro-1-methyl-5-isopropyltricyclo [5.1.1.0] octane (62).
Fig. 8: NMR spectrum of \textit{1,4,4,6,8,8-tetrachloro-1-methyl-5-isopropyl-tricyclo [5.1.1.0] octane} (62).
the each of two dienes by the results obtained. The results are consistent with those obtained from limonene (48)\textsuperscript{27,28} where in also the diadducts have been obtained exclusively. Further, this is in contrast to the results obtained from trans-isolimonene (50) where only mono adducts were obtained by previous workers\textsuperscript{29}.

**EXPERIMENTAL**

All the melting points were determined on a Gallenkamp apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer infracord instrument. NMR spectra (CDCl\textsubscript{3}/CCl\textsubscript{4}) were recorded on a varian A-60 spectrometer using TMS as an internal standard. Gas chromatography was carried on C.I.C. model (Baroda) gas chromatograph having dual column using nitrogen as carrier gas and a column of 10 percent DEGA on 30/60 chromosorp-P-NAW at 110\textdegree/160\textdegree.

**Starting materials**

All the reagents and solvents were obtained from commercial sources (B.D.H., E.Merck, S. Merck, Polyphorm) and were used without further purification. All the terpenoidal olefins except γ-terpinene were purified by column chromatography over silica-gel and checked by TLC and gas chromatography. r-Terpinene (Riedel, West Germany) was used without further purification.

Unless otherwise stated all the reactions were carried out in an inert atmosphere.
(i) Addition of dichlorocarbene to longifolene (55)

In a 250 ml round bottom flask was taken longifolene (55) (10.2 g), chloroform (50 ml) and triethyl benzylammonium chloride (1g). A 50 percent aqueous solution of sodium hydroxide (50 ml) was added dropwise at 55°C and the reaction mixture was continued to stirr for 5 hr. The reaction mixture was cooled and an excess of water was added. The organic layer was extracted with ether, washed with saturated solution of sodium chloride (100 ml), 5 percent sodium carbonate solution, water and dried over anhydrous sodium sulphate. The solvent was evaporated to obtain the crude reaction product (9.8 g) which was distilled under reduced pressure to separate the unreacted olefin (4.8 g) as evidenced by the comparison of IR spectra with that of an authentic sample of (55).

The residue (59) was chromatographed over silica-gel and elution with benzene-ethyl acetate (9:1) gave the addition product longibormyl-7-spiro-1'-{(2',2'-dichlorocyclopropane) (56) b.p. 140-1°/10 mm; yield : 3.8 g (50 percent). The product showed one spot on TLC and one peak in GLC.

Anal. data. found : C, 66.83; H, 8.8; Cl, 24.37 percent.

C_{16}H_{24}Cl_{2} requires : C, 66.89; H, 8.36; Cl, 24.73 percent.

IR spectrum (neat) : 1060, 1030, 830 and 735 cm\(^{-1}\).

NMR spectrum (CDCl\(_3\)) : \delta 0.65(2H, CH\(_2\)-CCl\(_2\)).

The compound did not decolourise bromine in carbon-tetrachloride and gave positive test for chlorine.
(ii) Addition of dichlorocarbene to isolongifolene (57)

The procedure as described above was followed. From isolongifolene (57) (10.2 g) there was obtained a crude reaction product (109) which was distilled under vacuum to recover the unreacted isolongifolene (4.49 g) as identified by comparison of IR spectrum with an authentic sample. The residue (5.6 g) was chromatographed over silica-gel (1:30) and elution with benzene-ethyl acetate (9:1) gave the addition product (58) b.p. 125°C/10 mm; yield: 4.2 g (51 percent). The compound showed one spot on TLC. Gas chromatography showed a broad band indicating that the product consists of two isomers which could not be separated.

**Anal. data** found: C, 66.93; H, 8.67; Cl, 24.98 percent
C_{16}H_{24}Cl_{2} requires: C, 66.89; H, 8.36; Cl, 24.73 percent.

**IR spectrum** (neat): 1030, 820, and 780 cm⁻¹

**NMR spectrum** (CCl₄): δ 0.65 (1 H, CH-CCl₂).

The compound (58) gave test for the presence of chlorine and did not decolourize bromine in carbon tetrachloride.

(iii) Addition of dichlorocarbene to terpinolene (59)

The procedure as described by Julia et al.²⁸ was followed. In a 250 ml round bottom flask fitted with a magnetic stirrer and reflux condenser was taken chloroform (100 ml), sodium hydroxide (209) and cetyl trimethyl ammonium bromide
(0.55g). To this mixture was added terpinolene (59) (9.52g) dropwise in 15 minutes. The reaction proceeded fast and was highly exothermic so the reaction flask was cooled by ice. The reaction mixture was further stirred for 1 hr. An excess of water was added and the organic phase was extracted with ether. The ether extract was washed with a saturated solution of sodium chloride followed by 5 percent solution of sodium carbonate, water and dried over anhydrous sodium sulphate. Removal of the solvent gave the crude reaction product (8.7g) which was distilled under vacuum to separate the unreacted olefin (1 g) as identified by the comparison of infrared spectra with that of an authentic sample of terpinolene (59). The residue (8.5 g) was chromatographed over silica-gel and elution with petroleum ether-genzene (1:1) furnished the addition product, trans-1-methyl-7,7-dichloronorcaran-4-spiro-(1',1'-dimethyl-2',2' dichlorocyclopropane) (60) b.p. 103°/10 mm, yield 6.8 g (35 percent). The compound gave one spot on TLC and gas chromatography showed one peak. The compound gave one spot on TLC and gas chromatography showed one peak.

**Analysis data** found: C, 47.75; H, 5.18; Cl, 46.68 percent
C<sub>12</sub>H<sub>16</sub>Cl<sub>4</sub> requires: C, 47.68; H, 5.29; Cl, 47.02 percent

**IR spectrum** (neat): 1030, 1005, 820 and 760 cm<sup>-1</sup>

**NMR spectrum** (C<sub>6</sub>D<sub>6</sub>): δ 0.68 (1H, CH-CCl<sub>2</sub>).

The compound gave a positive test for chlorine and did not decolourize bromine in carbon tetrachloride.
(iv) **Addition of dichlorocarbene to \( \gamma \)-terpinene (61)**

The procedure as described above was followed. From \( \gamma \)-terpinene (61) (9.52 g) there was obtained a crude reaction product which was distilled under vacuum to remove the unreacted olefin (0.5 g) as identified by the comparison of IR spectrum with an authentic sample of \( \gamma \)-terpinene (61).

The residue (9.0 g) on repeated crystallizations from chloroform-methanol gave a white crystalline compound, characterized as trans-4,4,8,8-tetrachloro-1-methyl-5-isopropyl tricyclo [5.1.1.0] octane (62) m.p. 82°C, yield 7g (35 percent). **

**Anal.data** found : C, 47.28; H, 5.09; Cl, 47.49 percent. 
C\(_2\)H\(_{16}\)Cl\(_4\) requires: C, 47.68; H, 5.29; Cl, 47.02 percent. 
IR spectrum (nujol) : 1030, 950, 815 and 760 cm\(^{-1}\). 
NMR spectrum (CCl\(_4\)) : \( \delta \) 1.22 and \( \delta \) 1.29 (CH.CCl\(_2\)).

The compound was saturated to bromine in carbon tetrachloride and gave positive test for chlorine.

The mother liquor obtained gave positive test for chlorine but decolourised bromine in carbon tetrachloride. TLC showed a mixed spot and gas chromatography indicated the product to be a mixture. Attempts to separate and characterise the components did not succeed.
REFERENCES