CHAPTER I

SOME SYNTHETIC AND COMPARATIVE STUDIES OF STABILIZED
AND NON-STABILIZED YLIDES

A GENERAL SURVEY

Ylides\(^1\) are Zwitterionic Compounds in which an anion is covalently bonded to a positively charged hetero-atom and are considered as resonance hybrids of two limiting structures, the ylide form (la) and the ylene form (lb). One of these, the ylide form (la) emphasizes the dipolar Zwitterionic nature involving anonium Centre at elements like nitrogen, phosphorus or sulfur, next to a carbanionic function which may atleast be partially delocalized in to suitable substituents. In the ylene form (lb), on the other hand, a true double bond is postulated between the onium centre and the ylidic carbon, thus reducing or even eliminating the formal charges at these atoms.\(^2,3\) The application of modern physical techniques and the results of sophisticated theoretical calculations\(^4,5\) have made it increasingly clear that the ylide form predominates in the ground state. Most of the early investigations successfully used this description for most of their problems of structure and reactivity and for the rationalization of reaction mechanism.\(^6\). Therefore, it is with justification that
the term ylide is used now-a-days almost exclusively in the literature.

The reactivity of the ylides depend upon the properties of the carbanion and on the possible involvement of the heteroatom. These compounds vary widely in stability, depending upon the symmetry of the molecule and the extent of \( \sigma^- - d_\pi \) bonding. A quantitative comparison of the stability of ylides, formed by different elements, have been made using the rates of alkali Catalyzed exchange of the \( \alpha \) -hydrogen atoms of the corresponding salts. The acidity of salt and hence the stability of the ylide is greatly affected by the change in structure.

Ylides have been classified in two main groups on the basis of stability and ease with which they undergo reaction with a variety of electrophilic substrates. The first and the larger group comprises of the ylides, called "non-stabilized ylides" which are generated in the solution from their corresponding salts but could not be isolated due to lack of the stabilizing factors and undergo reaction in situ. These ylides may further be divided in two categories depending upon the attachment of alkyl or aryl alkyl groups with the heteroatom. The arylalkyldene ylides, some times designated as semi-stabilized ylides which could not be isolated but persisted in solution for a considerable
time, in contrast to the alkylidene ylides which are very short-lived. The second and the smaller group consists of "Stabilized ylides" and is taken to imply an ylide which can be isolated, purified, usually stored in atmosphere and used in subsequent reactions. The stability of the these ylides is attributed to the attachment of the electron withdrawing groups with the ylidic carbanion.

In the recent years, the synthetic potentialities of ylides have been realized and studies on these reactive intermediates have been expanded in many directions which led to the exploration of the ylides of nitrogen, phosphorus and sulfur as evidenced by the research monographs and comprehensive review articles.

The involvement of a particular heteroatom results into marked differences in the chemical and physical behaviour of different type of ylides.

I.A. Azomethine ylides and their salts

On account of their remarkable and characteristic properties, the chemistry of pyridinium salts and their ylides having N-methyl or N-methylenes group, have generated a lot of interest. These ylides and salts form a special group of compounds having normal covalent bond between nitrogen and carbon atoms in which the free electron pair of the former can participate in N-C bond formation. As a result, the nitrogen atom is forced to approach
tetravalency (Scheme I.1). The pioneering work of Anderson in 1955 leading to the synthesis of ethylpyridinium iodide (2) by the interaction of pyridine with ethyl iodide (Scheme I.2) signalled the beginning of this type of compounds. A wide range of pyridinium salts has now been prepared, characterized and their chemistry thoroughly reviewed\textsuperscript{15,16,21,22}. The exploration of these salts and ylides\textsuperscript{23} has been and still is a challenge to the modern organic chemist.

F. Krohnke\textsuperscript{21,24} a German Chemist, deserves full credit for initiating his work in this all-important direction. He concentrated his attention on studying the reactivity of pyridinium salts and subsequently used them to synthesize a large variety of compounds. The reactivity of pyridinium salts is attributed to the aromatic character of the pyridine heterocycle, its basicity and to the electron withdrawing effect of the nitrogen atom in pyridine which becomes more pronounced in the azomethine ylides. In addition, the electrophilic effect of nitrogen renders positions 2, 4 and 6 of the heterocycle, relatively more electropositive. Thus, these positions become susceptible to the attack of nucleophiles. The electron deficiency at 2, 4 and 6 positions further activates the hydrogen atoms of methyl, benzyl or other groups attached to the α-carbon.
The abstraction of α-proton from N-methyl or N-methylenepyridinium salts, in presence of appropriate bases, result in the formation of highly reactive intermediates i.e. pyridinium ylides (Scheme I.3). These ylides are comparatively more reactive than the corresponding phosphonium ylides on account of the inability of the nitrogen atom to expand its valence shell electrons, thus precluding the existence of these ylides in the ylene form.

Azomethine ylides, obtained from their precursors, the so called pyridinium salts, are more stable on account of the extensive delocalization of the +ve charge on the pyridine ring as shown by various contributing forms (3a-d) (Scheme I.4) and the carbanion participation in the resonance of heteroaromatic ring (4a-c). The electrostatic interaction between the carbanion and onium group as represented in structure (7b), may also contribute towards greater stability. The lone pair of electrons associated with the sp³ hybridised ylidylic carbanions is involved in a IIId type of molecular orbital with sp² hybridised nitrogen atom of the pyridine ring. The extent of overlap increases if we take into consideration the resonating form (4c) which involves an interaction of bielectronic p orbital with the II electrons of the pyridine ring and hence the azomethine ylides are able to show greater stability. The stability of the azomethine ylides also depends upon the nature of substituents R¹ and R² attached to the carbanion. In the event of these groups being electron withdrawing in nature, additional resonance structures are possible involving a marked sp² hybridization of ylide carbon through charge delocalization.⁷
I.A.1 Preparation of pyridinium salts, precursors of azomethine ylides

A.1.1 By action of organic halides and esters with pyridine

The reaction of pyridine with organic halides (5) such as α-haloesters, α-haloketones or α-halonitriles in polar solvents forms quaternary pyridinium salts (6). The reaction involves the displacement of the halogen as halide ion by pyridine which acts as a nucleophile (Scheme I.5). Investigations have revealed that the rate of reaction with alkyl halides decreases in the order I > Br > Cl (24, 25).

A.1.2 By Ortoleva King Method

King et al (26-28) have reported a direct method for the preparation of pyridinium salts by heating active methyl or methylene compounds (7) with iodine in pyridine. Ortoleva (25) was the first to apply this method. Later on, King and others successfully used it in number of cases. Now this method which came to be known as Ortoleva-King method, forms N-substituted pyridinium iodide (8) (Scheme I.6). Since pyridine also serves as a solvent, it is used in sufficient excess. The method affords excellent yields.
Scheme 1.1

\[ \text{Scheme 1.1} \]

Scheme 1.2

\[ \text{Scheme 1.2} \]

Scheme 1.3

\[ \text{Scheme 1.3} \]

Scheme 1.4

\[ \text{Scheme 1.4} \]
A.1.3. By the reaction of diazoketones with pyridine hydroiodide

The reaction of diazoacetophenone(9) with pyridinium hydroiodide salt yields phenacylpyridinium iodide(11). The reaction seems to proceed via the formation of carbene intermediate(10)\textsuperscript{29}(Scheme I.7).

A.1.4 By the reaction of Tosyl chloride with pyridine

The reaction of tosyl chloride on alcohol yields alkyl sulphonates which, on treatment with pyridine, lead to the formation of quaternary pyridinium salts\textsuperscript{(12)}\textsuperscript{30}(Scheme I.8).

A.1.5 By transformation of other pyridinium salts

The reaction of 1-methylpyridinium salts with benzaldehyde in alcohol containing piperidine to form 1-(α-hydroxyphenylethyl) pyridinium salt\textsuperscript{(13)}(Scheme I.9) was studied by Krohnke et al\textsuperscript{31,32}. This salt\textsuperscript{(13)} has also been synthesised by the reaction of phenacylpyridinium bromide\textsuperscript{(14)} with benzaldehyde at 0°C in presence of piperidine or dimethylamine\textsuperscript{33}(Scheme I.9).

I.A.2 Generation of azomethine ylides

A.2.1. Ylides from pyridinium salts(Salt Method)

The most common method used for the preparation of pyridinium ylides\textsuperscript{(15)} involves the action of a base on quaternary pyridinium salts\textsuperscript{24}(Scheme I.10). The nature of the desired ylide entirely determines the choice of reaction conditions in which they are easily
Scheme I.5

\[
\begin{align*}
C_5H_5N + X-CH & \quad \rightarrow \quad C_5H_5N-CH_xR^1R^2 \\
\text{Scheme I.6} & \quad \rightarrow \quad C_5H_5N-CH_2COR_1^x + C_5H_5NH_1
\end{align*}
\]

Scheme I.7

\[
\begin{align*}
C_5H_5N + X-CH & \quad \rightarrow \quad C_5H_5N-CH_2COCH_1 + C_5H_5NH_1 \quad \rightarrow \quad C_5H_5N-CH_2COCH_1 + C_5H_5NH_1
\end{align*}
\]
generated. The strength of the base required for the dehydrohalogenation of the pyridinium salts, is directly related to the acidity of the α-hydrogen atom which itself is dependent upon the nature of substituents linked to the β-carbon atom. Most common bases used for this purpose are aqueous solution of alkali carbonates\textsuperscript{24} or amines in anhydrous aprotic solvents\textsuperscript{24,34,35}. Sometimes the use of sodium hydride in dimethylformamide have also been found advantageous\textsuperscript{34,35}. A large number of pyridinium ylides can not be isolated on account of their sensitivity towards atmospheric components. Such ylides are, therefore, prepared in anhydrous solvents under inert atmospheric conditions\textsuperscript{36}. Thus, the reaction may be carried out in non-polar solvents like benzene. However, sometimes, a polar solvent is found to be more advantageous\textsuperscript{21,26}.

A.2.2. Ylides from Pyridine and Ethylene Oxide

Linn et al\textsuperscript{37} and others\textsuperscript{38} have prepared a stable high melting pyridiniumdicyanomethylide(16) by the reaction of pyridine with tetracyanoethylene oxide at 0°C(Scheme I.11)

A.2.3 Ylides from Diazoc compounds and Pyridines

The irradiation of tetraphenyl or triphenyldiazocyclopentadiene in pyridine under inert nitrogen with a high pressure of mercury lamp through a pyrex filter also yields pyridinium ylides(17)\textsuperscript{39}(Scheme I.12).
A.2.4 Ylides from other azomethine ylides

Lionte and Zugrovescu\(^{40}\) have synthesized di-
cyanopyridiniummethylide(19) by heating cyanocarbamylpy-
ridiniummethylide(18) with PCl\(_3\) in presence of sodium 
pyrosulphite. However, on using acetic anhydride as 
dehydrating agent, cyanoacetylpypirdinium methylide(20) 
was obtained. The ylide(20) may also be prepared by 
acetylation of ylide(21). The ylide(19) may also be 
synthesized by the reaction of bromocyano acetic ester 
with carbalkoxytpyridinium ylide(22) (Scheme I.13).

I.A.3. Reactivity of azomethine ylides and their salts

A.3.1. Alkylation

Azomethine ylides, prepared by the action 
of a base on its precursor, yield C-alkylated pyridinium 
salts alongwith alkyl halides. The salts, thus formed, 
react with suitable bases to give carbanion-disubstituted 
ylides(23)\(^{41}\) (Scheme I.14). This reaction is not applic-
able for the synthesis of the type(23) as the ylides 
undergo decomposition.

If, however, a dehydrohalogenating agent is 
present during the alkylation, a series of products 
are formed. Thus pyridiniumphenacyl ylide(24) with phenacyl 
bromide, yields several products with different struct-
tures(26,27) possibly due to interaction between the 
intermediate(25) and the initial ylide(24) and also 
to the transylidation and bond breaking\(^{33}\) (Scheme I.15).
Scheme I.9

\[ R-\text{CH}_2\text{O}-\text{H} + \text{CH}_3-\text{SO}_2\text{Cl} \rightarrow R-\text{CH}_2\text{O}\text{SO}_2-\text{CH}_3 \]

\[ \text{T}_s = \text{CH}_3-\text{SO}_2 \]

\[ \text{C}_5\text{H}_5\text{N} \cdot \text{CH}_2\text{R} \cdot \text{T}_s^\text{O} \]

Scheme I.9

\[ \text{CH}_3 + \text{O}=\text{CH} \rightarrow \text{PhCOO}^\text{+} \text{CH}=\text{O} + \text{Ph} \]

\[ \text{H-C-OH} \]

\[ \text{13} \]

\[ \text{14} \]

Scheme I.10

\[ \text{ON}^\text{+} - \text{CH}_2 - \text{R} \xrightarrow{\text{Base}} - \text{HX} \]

\[ \text{ON}^\text{+} - \text{CH} - \text{R} \]

\[ \text{15} \]

Scheme I.11

\[ \text{ON} + (\text{CN})_2 \xrightarrow{} \text{C} - \text{C} (\text{CN})_2 \]

\[ \text{16} \]

Scheme I.12

\[ \text{Ph} \]

\[ \text{Ph} \]

\[ \text{Ph} \]

\[ \text{Ph} \]

\[ \text{Ph} \]

\[ \text{Ph} \]

\[ \text{R} \]

\[ \text{N} \]

\[ \text{R} \]

\[ \text{17} \]
A.3.2 Acylation

On account of the strong nucleophilic nature of the ylide carbanion generated during the course of the reaction, acylation of azomethine ylide may be brought about in a facile manner, using acyl halide or acetic anhydride. Thus, the reaction of phenacylpyridinium bromide(28) with benzoyl chloride in presence of potassium carbonate, produces acetylated azomethine ylides(29)\(^{42}\) (Scheme I.16). It may be noted that the acylation of carbonyl stabilized ylides(30 a-b) with benzoyl chloride leads to a O-acylated(31a) and S-acylated ylides (31b)\(^{42}\) (Scheme I.17) whereas, acylation with benzoic anhydride takes different course to give C-acylated products(32 a-b)\(^{34,35}\) (Scheme I.17). Likewise, reaction of phenylisocyanate with ylides(30 a-b) follows the C-acylation and forms a new ylide (33 a-b) which, on proton transfer, yields a new azomethine ylide(34 a-b)\(^{43}\) (Scheme I.17).

A.3.3 Arylation

On account of the low reactivity of aryl halides, arylation of pyridinium salts and ylides is a comparatively more difficult reaction. The reaction of picryl chloride with phenacylpyridinium bromide in basic medium forms a product(35) which, in strong alkaline medium, eliminates nitrous acid to yield a deep red indolizine compound(36) which itself is a benzoyl
Scheme I.13

\[
\text{C}_5\text{H}_5\text{N}^+\underset{\text{CN}}{\text{C}}\overset{\text{CN}}{\text{C}} \xrightarrow{19} \text{Br}\underset{\text{CN}}{\text{CH}}\overset{\text{COOR}}{\text{COOR}}
\]

\[
\text{C}_5\text{H}_5\text{N}^+\underset{\text{CN}}{\text{C}}\overset{\text{CN}}{\text{CONH}_2} \xrightarrow{18} \text{C}_5\text{H}_5\text{N}^+\underset{\text{CN}}{\text{C}}\overset{\text{COCH}_3}{\text{Ac}_2\text{O}}
\]

\[
\text{Et}_3\text{N}/\text{C}_5\text{H}_5\text{N} \xrightarrow{20} \text{C}_5\text{H}_5\text{N}^+\underset{\text{CH}_2\text{-CN}}{\text{Cl}}
\]

Scheme I.14

\[
\text{C}_5\text{H}_5\text{N}^+\underset{\text{C}}{\text{CH}}\overset{\text{CHR}}{\text{R}} + \text{R}^{'-}\text{X} \xrightarrow{\text{Ylide}} \text{C}_5\text{H}_5\text{N}^+\underset{\text{C}}{\text{CH}}\overset{\text{R}}{\text{R}} \xrightarrow{\text{Base}} \text{C}_5\text{H}_5\text{N}^+\underset{\text{C}}{\text{CH}}\overset{\text{R}}{\text{R}}\xrightarrow{-\text{HX}} \text{C}_5\text{H}_5\text{N}^+\underset{\text{C}}{\text{CH}}\overset{\text{R}}{\text{R}}
\]

Scheme I.15

\[
\text{C}_5\text{H}_5\text{N}^+\underset{\text{CH}}{\text{CH}}\overset{\text{COC}_6\text{H}_5}{\text{C}} + \text{C}_6\text{H}_5\text{COCH}_2\text{-Br} \xrightarrow{24} \text{C}_5\text{H}_5\text{N}^+\underset{\text{CH}}{\text{CH}}\overset{\text{COC}_6\text{H}_5\text{Br}}{\text{C}}\overset{\text{CH}_2\text{COC}_6\text{H}_5}{\text{C}}
\]

\[
\text{C}_6\text{H}_5\text{COCH}=\text{CH}\overset{\text{+24}}{\text{CO}}\overset{\text{-HBr}}{\text{-C}_6\text{H}_5} \xrightarrow{\triangle} \text{C}_5\text{H}_5\text{N}^+\underset{\text{C}}{\text{CH}}\overset{\text{COC}_6\text{H}_5}{\text{C}}\overset{\text{CH}_2\text{COC}_6\text{H}_5}{\text{C}}
\]

\[
\text{C}_5\text{H}_5\text{N}^+\underset{\text{CH}}{\text{CH}}\overset{\text{CH}}{\text{CH}}\overset{\text{COC}_6\text{H}_5}{\text{C}}\overset{\text{CH}_2\text{COC}_6\text{H}_5}{\text{C}} \xrightarrow{\triangle} \text{C}_6\text{H}_5\text{COO}_{\text{C}_6\text{H}_5}
\]

\[
\text{C}_6\text{H}_5\text{COO}_{\text{C}_6\text{H}_5} \xrightarrow{-\text{C}_5\text{H}_5\text{N}} \text{C}_6\text{H}_5\text{CO}_{\text{C}_6\text{H}_5}
\]

27
Scheme I.16

\[
\begin{align*}
C_5H_5N^+ - CH_2COR & \xrightarrow{\text{Br}} C_5H_5N^+ - CHCOR \\
& \xrightarrow{-\text{HBr}} C_5H_5N^+ - CHCOR \\
& \xrightarrow{\text{Base}} C_5H_5N^+ - CHCOR \\
& \xrightarrow{-\text{HX}} C_5H_5N^+ - CHCOR
\end{align*}
\]

28

Scheme I.17

\[
\begin{align*}
C_5H_5N^+ - CH=CHSCH_3 & \xrightarrow{\text{Cl}} C_5H_5N^+ - CH-C-SCH_3 \\
& \xrightarrow{\text{XCOC}_6\text{H}_5} C_5H_5N^+ - CH-C-SCH_3
\end{align*}
\]

31a-b

(30, 31a $\rightarrow X=0$ & 30, 31b $\rightarrow X=S$)

30a-b

\[
\begin{align*}
\text{(PhCO)}_2O & \xrightarrow{\text{C}_5\text{H}_5N^+ - C - CXCH}_3 \xrightarrow{\text{COC}_6\text{H}_5} C_5\text{H}_5N^+ - C - CXCH}_3 \xrightarrow{\text{PhNCO}} C_5\text{H}_5N^+ - CH(CONPh) \xrightarrow{\Delta} C_5\text{H}_5N^+ - C - CXCH}_3 \xrightarrow{\text{CONPh}}
\end{align*}
\]

32a-b

33a-b

34a-b
group on heating in acetic medium to form a product \(37\)^44(Scheme I.18).

N-phenacylpyridinium bromide\(28\) may also similarly react with chloranil to form a zwitterion which undergoes cyclisation to yield indolizines\(38\) and \(39\)^44(Scheme I.19).

A.3.4 Reaction with aldehydes

The azomethine ylide\(40\) reacts with aldehydes to form pyridinium ethanolos\(41\)^45(Scheme I.20). However, in case, an acyl radical is attached to the ylide, it is cleared during the condensation with aldehyde to yield the pyridinium salt \(42\)^46(Scheme I.21). In presence of pyridine, aromatic aldehydes react with pyridinium salt\(43\) with strong electron withdrawing substituents to afford vinyl pyridinium salt\(44\)(Scheme I.29). However, aromatic aldehydes bonded with electron donating groups, react with acylimethylpyridinium salt\(28\) at boiling temperature and in presence of acetic anhydride to form vinyl pyridinium salts\(45\)^46(Scheme I.23).

In the presence of glacial acetic acid with ammonia phenacylpyridinium bromide reacts with aromatic aldehydes bonded to a substituent with (-I) effect, to form 2,4,6-triarylpyridines\(46\) through Mannich type of reaction\(^47\)(Scheme I. 24).

A.3.5 Reaction with Ketones

2-Chloro-1,4-naphthoquinone reacts with phen-
acylpyridinium bromide, following Michael addition, to form a stable substituted phenacylphthoquinone(47) which itself undergoes cyclization to form benzocoumarin (48) in presence of zinc and acetic acid and with hydrazine hydrate, benzocinnoline(49) is formed$^{48,49}$ (Scheme I.25). Aliphatic ketones yield Aldol type of products(50) (Scheme I.26) when reached with tropone, yields 2-hydroxy-1-2-phenyl-3-phenacyl-2H cyclohepta(b) furan(51)(Scheme 1.27)$^{50}$.

A.3.6. Reaction with $\alpha,\beta$ unsaturated Ketones

The pyridinium salts react with $\alpha,\beta$-unsaturated ketones in a variety of ways to yield different products. The nature of the product of the reaction depends of the experimental conditions as well as on the substituents attached to the pyridinium salts. For example, aroylmethylpyridinium salts(52) readily add on $\alpha,\beta$-unsaturated ketones to undergo Michael addition forming pentane-1, 5-dionolpyridinium derivatives(53) which, in presence of a mixture of glacial acetic acid and ammonium acetate, undergo azo ring closure to form 2, 4, 6-triarylpirdines(54)$^{51,52}$ (Scheme I.28). However, Theasing and Muller have synthesized 2-pyridones(55 & 56) by the Michael addition of N-(aminoformylmethyl)pyridinium chloride onto Mannich bases or $\alpha,\beta$-unsaturated ketones$^{53,54}$ (Scheme I.29).
Scheme I.26

\[
\text{C}_5\text{H}_5\text{N}^+\text{CH}_2\text{R} + \text{O} = \text{C}_2^+\text{R}_1^+\text{R}_2^+ \xrightarrow{\text{HBr}} \left[ \text{C}_5\text{H}_5\text{N}^+\text{CH}-\text{C}-\text{R}_1^+\text{R}_2^+ \right] \text{Br}^- \quad 50
\]

Scheme I.27

\[
\text{C}_5\text{H}_5\text{N}^+\text{CH-COR} + \text{phenyl} \rightarrow \text{compound} \quad 51
\]

Scheme I.28

\[
\text{C}_5\text{H}_5\text{N}^+\text{Br}^- + \text{compound} \rightarrow \text{compound} \quad 53
\]

\[
\text{NH}_4\text{OAc/} \quad \text{AcOH}
\]

\[
\text{compound} \quad 54
\]
Benzylpyridinium bromide reacts with benzalacetophenone to form 1,3-diphenynaphthalene(58)\textsuperscript{22}(Scheme I.30). Recently, Tewari et al\textsuperscript{55} has utilized this reaction in the synthesis of a wide variety of naphthalenes.

A.3.7. Reaction with Nitroso compounds

Azomethine ylides react with nitroso compounds in a manner analogous to that of the sulphur ylides\textsuperscript{56}. Krohnke et al\textsuperscript{56} were the first to investigate the reaction of phenacylpyridinium ylide with nitrosobenzene to yield α-benzoyl-N-phenylnitrones(59)(Scheme I.31) which find numerous applications in synthetic organic chemistry on account of their ability to form carbonyl compounds on undergoing acid hydrolysis. On the other hand, the elimination-addition reactions of 4-bromophenacylpyridinium ylide(60) with α-nitroso-3-naphthols and α-nitroso-3-naphthylamine gave naphthoxazole derivatives(61) and benzoquinoxaline-N-oxide derivatives(62) respectively\textsuperscript{57}(Scheme I.32).

A.3.8. Reaction with Isocyanates and Isothiocyanates

The reaction of phenacylpyridinium ylide with phenylisocyanate(63a) and isothiocyanate(63b) separately to afford 2-(α-phenyl carbamoylphenacyl) pyridinium betaine(64) and 2-(α-phenylthiocarbamoylphenacyl) pyridinium betaine(65) respectively\textsuperscript{57,58-60}(Scheme I.33).

A.3.9. Reaction with Carbon-sulfur bond

The reaction of phenacylpyridinium ylide,
when treated with carboxysulphide, affords sulphur containing betaine(66) which reacts with methyl iodide to yield an alkylated product(67)\textsuperscript{42,57}(Scheme I.34).

A.3.10. 1,3-Dipolar cycloaddition Reaction

Azomethine ylides, due to delocalization of +ve charge over pyridine ring, form 1,3-dipolar systems. Thus, these systems may react with a variety of dipolar ophiles to afford(3 + 2) cycloadducts which, on dehydrogenation with palladium and charcoal, give indolizine derivatives(68)\textsuperscript{61-66}(Scheme I.35).

A.3.11 Reactions with Aromatic amines

Krohnke et al\textsuperscript{67} have reported the reaction of N-phenacylpyridinium ylides with 0 and p-toluidines in presence of dimethylamine to give substituted indole derivatives(69). Recently, Bansal et al\textsuperscript{68} has exploited this reaction in the synthesis of a wide variety substituted indoles(Scheme I.36). However, the reaction of azomethine ylide and o-phenylenediamine in boiling acetic acid gives 2-phenylbenzimidazole(70)\textsuperscript{51,67}(Scheme I.37).

A.3.12. Reduction of azomethine ylides

Reduction of al-kylated and acylated azomethine ylides with zinc and acetic acid gives ketones(71) and diketones(72)\textsuperscript{58,61}(Scheme I.38).

A.3.13. Thermolysis of azomethine ylide

The literature reveals that little information is available regarding the thermal stability of the
Scheme 1.29

C₅H₅N⁺CH

O=CNH₂

Ph-CH

CH-C-Ph

↓

C₅H₅⁺Ph

C₅H₅NH

Ph

O=CNH

Ph

C₅H₅⁺Ph

Me₂N-CH₂-CH₂-C-Ph

↓

Scheme 1.30

C₅H₅N⁺CH₂

Br⁻

Ph

+ \text{CH=CH} \text{O=C-R}^1

\rightarrow

C₅H₅N⁺CH

CH-CH

\text{O=C-R}^1

R

\text{ZnCl}_2

200 °C

58

57
Scheme I.31

\[ \text{C}_5\text{H}_5\text{N}^\oplus \text{CH}^- \text{COPh} + \text{PhN}=\text{O} \rightarrow \text{Ph}^+=\text{N}^-\text{N}^-\text{COPh} \]
\[ \downarrow \text{O} + \text{C}_5\text{H}_5\text{N} \]

Scheme I.32

\[ \text{C}_5\text{H}_5\text{N}^-\text{CH}^+\text{CO}\cdot\text{C}_6\text{H}_4^-\text{Br} + \]
\[ \text{HO} \downdownarrows \text{NO} \]
\[ \text{CH}^-\text{COC}_6\text{H}_4\text{Br} \]
\[ \rightarrow \text{N}^-\text{C}^-\text{COC}_6\text{H}_4^-\text{Br} \]
\[ \downarrow \text{H}_2\text{O} \]
\[ \text{N}^-\text{C}^-\text{COC}_6\text{H}_4^-\text{Br} \]
\[ \rightarrow \text{N}^-\text{C}^-\text{COC}_6\text{H}_4^-\text{Br} \]
\[ \downarrow \text{H}_2\text{O} \]
\[ \text{N}^-\text{C}^-\text{COC}_6\text{H}_4^-\text{Br} \]
Scheme I.33

\[ \text{C}_5\text{H}_5\text{N}^-\text{CH}^-\text{COC}_6\text{H}_5^- + \text{C}_6\text{H}_5\text{N}=\text{C}=\text{X} \overset{63 \text{ a-b}}{\longrightarrow} \text{C}_5\text{H}_5\text{N}^-\text{C}^-\text{COC}_6\text{H}_5 \]

\[ \text{X}^-\text{C}^-\text{NH}_2\text{C}_6\text{H}_5 \]

64, \( X = 0 \)

65, \( X = 0 \)

Scheme I.34

\[ \text{C}_5\text{H}_5\text{N}^-\text{CH}^-\text{COC}_6\text{H}_5^- + \text{C}=\text{S} \overset{66}{\longrightarrow} \text{C}_5\text{H}_5\text{N}^-\text{CH}^-\text{COC}_6\text{H}_5^- \]

\[ \text{CH}_3\text{I} \]

\[ \text{C}_5\text{H}_5\text{N}^-\text{CH}^-\text{COC}_6\text{H}_5^- + \text{C}=\text{S} \overset{67}{\longrightarrow} \text{C}_5\text{H}_5\text{N}^-\text{CH}^-\text{COC}_6\text{H}_5^- \]

Scheme I.35

\[ \text{(Diagram showing reaction involving R, R', and R'' groups)} \]

\[ \overset{\text{Pd/c}}{\longrightarrow} \text{R} \]

68
Scheme I.36

\[
\text{Scheme I.37}
\]

\[
\text{Scheme I.38}
\]

\[
C_{5}H_{5}N - C_{\text{COR}} + \text{Zn} / \text{AcOH} \rightarrow C_{5}H_{5}N + \text{R-CH}_{2}\text{-COR}
\]

\[71, R = \text{Alkyl} \]

\[72, R = \text{Aroyl} \]
azomethine ylides and their precursors. Cook et al.\textsuperscript{69} have, however, been able to isolate dibenzoylethylene(74) by sublimation of phenacylpyridinium ylide under greatly reduced pressure. It appears that the product(74) was formed by the dimerisation of carbene intermediate(73) which itself resulted from the heterolytic cleavage of N-C bond of ylide(Scheme I.39). The thermolysis of ylide or its precursor in benzene and in presence of copper oxide yields an unexpected product, 1,3-dibenzoylindolizine(75)\textsuperscript{61,69}(Scheme I.39).


Very little work has been done on the photolytic conversion of azomethine ylides. The irradiation of pyridiniumdicyanamethylide in benzene solution by ultraviolet light, reported by Streith et al.\textsuperscript{70} results in the formation of a pyrrole derivative(77) and dicyano-carbadiene(78)(Scheme I.40). The first(77) of the two products is probably formed by the contraction of the pyridine ring while the other(78) appears to have been formed by the attack of dicyanocarbene intermediate(76) on benzene.

A.3.15. Reaction of azomethine salts and ylides with aryl diazonium salts

Recently, Bansal et al.\textsuperscript{71} have developed a new route for the synthesis of 1,4-dihydro-1,2,4,5-tetra-
zines(80) which have been formed by the reaction of phenacylpyridinium ylides(79) with aryldiazonium salts in presence of cold solution of sodium acetate(Scheme I.41).

I.B. Phosphonium ylides and their Precursors

In the later half of 1940, Wittig\(^7\) investigated the existence of compounds of pentavalent nitrogen and discovered the nitrogen ylide of the type(82) which was prepared by the action of phenyl lithium on tetramethylammonium salt(81). Formulation of the nitrogen ylides(82) was proved by the addition of benzophenone(83) to yield (2-hydroxy-2,2-diphenyl) trimethylammonium salt(84)(Scheme I.42). Later on, he extended his studies to phosphorus, the next higher element of group V. His attempt to prepare stereoisomers of pentaphenyl phosphorus compound led to the first synthesis of crystalline methylenetriphenylphosphorane(85). This product, as Wittig\(^7\) and his coworker observed, reacts with benzophenone(83) to give almost quantitatively, 1,1-diphenylethynelic(86) and triphenylphosphine oxide(Scheme I. 42).

The phosphonium ylides have been found to be generally more stable than the nitrogen ylides. The overlap of the doubly occupied 2p orbital of the ylide carbon with the unoccupied 3d orbital of phosphorus atom and can be represented by the resonance hybrid of two limiting structures, the ylide form(87a) and
the ylene form(87b). A similar conjugation is not possible with nitrogen ylides due to lack of d orbital in nitrogen atom. The stability of the phosphorus ylides is due, mainly, to the possibility of the 3d orbital of phosphorus forming actual π bond.74 This is exactly why comparatively larger number of phosphorus ylides have been isolated and characterised as stable species.75-84.

On the basis of their reactivity, phosphonium ylides have been divided into two main groups. The first and the larger group contains the alkylidene phosphoranes of low stability and high reactivity while the second group includes highly stable unreactive resonance stabilized phosphoranes.

The phosphonium ylides are capable of undergoing two basic types of reactions, those in which only the ylide carbanion is mechanistically involved and those in which both the ylide carbanion and the heteroatom part are involved. The reactivity of alkylidene phosphorane is determined by the distribution of the negative charge in the molecule, which itself is dependent upon the nature of the substituents \( R^1 \) and \( R^2 \) in the alkylidene portion as well as on the group \( R \) on phosphorus. Thus, if the lone pair of electrons on the \( \alpha \)-carbon atom of the ylide form(87a) is delocalised over the groups \( R^1 \) and \( R^2 \), the nucleophilic nature of the
phosphorane decreases and the stability increases. The election withdrawing substituents $R_1^1$ and $R_2^1$ stabilize the negative charge and hence reduce the reactivity of the ylide. In the absence of any such interaction, an extremely reactive and unstable ylide is formed.

The reaction has since come to be known as the Wittig reaction or Wittig olefination and has been instrumental in initiating extensive original research to meet the challenge of establishing its preparative potential and the study of its mechanistic aspects.

I.B.2 Preparation of phosphonium ylides and their salts

B.2.1 Ylides from Phosphonium salts

Quaternary phosphonium salts(88), obtainable from trialkyl or triarylphosphines and alkyl halides, on reaction with appropriate bases, yield phosphonium ylides(89)$^{74}$ (Scheme I.43). The reaction is usually carried out in a non-polar solvent such as benzene, though sometimes a more polar solvent is advantageous. The strength of base required for deprotonation of phosphonium salts depends upon the acidity of phosphonium salts and more specifically on the substituents $R_1^1$ and $R_2^1$ on the ylide carbonion bases such as ammonia$^{85}$, triethylamine$^{86,87}$, pyridine$^{88,89}$, sodium hydride$^{90}$, sodium ethoxide$^{91}$, sodamide$^{92}$, potassium ter-butoxide$^{93}$, lithium piperide$^{92}$, butyl lithium$^{94}$ and phenyl lithium$^{95}$.
Scheme I.42

\[
(\text{CH}_3)_4 N^+ X^- + C_6 H_5 Li \rightarrow C_6 H_6 + (\text{CH}_3)_3 N^- \text{CH}_2 + \text{Li} X^- 
\]

81

\[
6 + (C_6 H_5)_2 \text{C}=\text{O} \rightarrow (C_6 H_5)_2 \text{C}-\text{CH}_2-\text{N}(\text{CH}_3)_3 X^- 
\]

83

Scheme I.42a

\[
\text{Ph}_3 P^- \text{CH}_2 + (C_6 H_5)_2 \text{CO} \rightarrow (C_6 H_5)_2 \text{C}=\text{CH}_2 + \text{Ph}_3 \text{PO} 
\]

85

86

87a

87

87b

Scheme I.43

\[
R_3 P + \text{Br}-\text{CH}_2 R_1 R_2 \rightarrow R_3 P-\text{CH}_2 R_1 R_2^\text{Br}^+ 
\]

88

Base

\[
R_3 P=\text{C}_2 R_1 R_2 \rightarrow R_3 P-\text{C}_2 R_1 R_2 
\]

89
have usually been utilized.

B.2.2. *Ylides from carbenes and Triphenylphosphine*

Phosphonium ylides may also be prepared by the reaction between carbon tetrachloride or carbontetra-bromide and triphenylphosphine\(^96,97\) (Scheme I.44). It is also possible to use diazoliphates\(^91\) as source of carbene for the preparation of phosphonium ylides\(^92\). However, for this reaction to occur, the diazoaliphatics should be decomposed in presence of Cu(I) salt. Generally triphenylphosphine reacts with diazo compounds to form phosphazine\(^98\) (Scheme I.45).

B.2.3. *Ylides from Phosphine and activated multiple bond*

Phosphonium ylides\(^94\) can also be synthesized by the interaction of triarylphosphine with a compound associated with multiple bond having electron withdrawing substituents\(^96,99,100\) (Scheme I.46).

B.2.4. *Ylides by Pyrolysis of Phosphonium salt*

The thermally less stable phosphonium salt \((95)\) on pyrolysis yields stable ylides\(^96\)\(^101\) (Scheme I.47).

B.2.5. *Ylides from Vinyltriphenylphosphonium salt*

The phosphonium ylides\(^98\) can also be synthesized by the action of phenyl lithium on vinyltriphenylphosphonium bromide\(^97\)\(^102\) (Scheme I.48).

B.2.6. *Ylides from active methylene compounds*

When dihalotriphenylphosphine\(^99\) is heated
with active methylene compounds(100) in presence of teramine, phosphonium ylide(101) is directly formed\textsuperscript{103} (Scheme I.49).

B.2.7. **Ylides from Benzyne Intermediate**

Benzyne intermediate(102) because of its reactivity, quickly couples with tryalkyl or triarylphosphine to give ylide(104). The reaction is supposed to occur via a 1,3-dipolar intermediate(103) which rearranges to afford reactive ylide(104)\textsuperscript{104} (Scheme I.50).

B.2.8. **Ylide by the action of Triflates on Triarylphosphine**

Recently, synthesis of ylides have been achieved by the reaction of triphenylphosphine and reactive triflates(105) to give phosphonium salts(106) which on treatment with base DBU afforded ylides(107)\textsuperscript{105} (Scheme I.51).

B.2.9. **Ylides from Transylation**

A wide variety of complex and stable ylides which are difficult to be prepared by the conventional method, have been prepared by the method so called transylation\textsuperscript{106}. This method which involves the interaction of two moles of non-stabilized ylide(108) with one mole of alkyl or acyl halide to afford carbonyl stabilized phosphonium ylide(110), has gained extensive application in preparation of stabilized ylides(110)\textsuperscript{106-110} (Scheme I. 52).

I.B.3. **Reactions of Phosphonium ylides**
Scheme 1.44

\[ \text{Ph}_3\text{P} + \text{CX}_4 \rightarrow \text{Ph}_3\text{P} = \text{CX}_2 + \text{Ph}_3\text{PX}_2 \]

\[ \text{X} = \text{Cl, Br} \]

Scheme 1.45

\[ \text{Ph}_3\text{P} + \text{N} \equiv \text{N} - \text{C} \rightarrow \text{Ph}_3\text{P} = \text{N} \equiv \text{N} - \text{C} \quad \text{(91)} \]

\[ \text{Ph}_3\text{P} = \text{N} \equiv \text{N} - \text{C} \quad \text{(93)} \]

Scheme 1.46

\[ \text{Ph}_3\text{P} + \text{C} = \text{C} - \text{R} \rightarrow \text{Ph}_3\text{P} = \text{C} - \text{C} - \text{R} \quad \text{(94)} \]

\[ \text{R} = \text{COOR}^1, \text{CONH}_2, \text{CN} \quad \text{etc.} \]

Scheme 1.47

\[ \text{R} - \text{C} = \text{C} - \text{OR}^1 \quad \text{(95)} \]

\[ \xrightarrow{\Delta} \text{R} - \text{C} = \text{PPh}_3 + \text{CO}_2 + \text{HX} \quad \text{(96)} \]
Scheme I.48

\[ \text{Ph}_3\text{P} - \text{CH}=\text{CH}_2 \xrightarrow{\text{Ph}_3\text{P} - \text{C}_6\text{H}_5\text{Li}} \text{Br} \xrightarrow{\Theta} \text{Ph}_3\text{P} - \text{CH}-\text{CH}_2 - \text{C}_6\text{H}_5 \]

Scheme I.49

\[ \text{Ph}_3\text{PX}_2 + \text{H}_2\text{C} - \begin{array}{c} \text{R}_1 \\ \text{R}_2 \end{array} \xrightarrow{\text{NR}_3 - 2\text{HX}} \text{Ph}_3\text{P} = \begin{array}{c} \text{C} \\ \text{R}_1 \\ \text{R}_2 \end{array} \]

Scheme I.50

\[ \text{Ph}_3\text{P} + \text{Ph}_2\text{P}-\text{CH}_3 \xrightarrow{\Theta} \text{Ph} \xrightarrow{\Theta} \text{Ph} \xrightarrow{\Theta} \text{Ph} \]

Scheme I.51

\[ \text{Ph}_3\text{P} + \text{CH}_2=\text{C(OTE)}\text{CH}_2\text{OT}_f \xrightarrow{\Theta} \text{CH}_2=\text{C(OTE)}\text{CH}_2 - \text{PPh}_3 \text{OT}_f \]

\[ \xrightarrow{\Theta} \]

\[ \text{DBU} \]

\[ \text{CH}_2=\text{C(OTE)}\text{CH}=\text{PPh}_3 \]
Ylides as defined earlier, are the unique form of carbanions and undergo reaction with a wide variety of electrophilic reagents. The unique behaviour of ylide carbanion is due to its ability of phosphorus to become pentavalent. That is why ylide carbanions exhibit some typical reactions which are not expected from simple carbanion. Some interesting and useful reactions of phosphonium ylides have been illustrated in the following categories.

B.3.1. Ylide and salt as Bronsted Acid base pair

Phosphonium ylides derived from their precursors, phosphonium salts, by dehydrohalogenation, are able to be attacked by hydrogen halide, whereby original salt is regenerated. Therefore, phosphonium salts may be considered as Bronsted acids and the phosphonium ylide as Bronsted base(Scheme I.53).

B.3.2. Oxidation of Phosphonium Ylide

Action of oxygen on phosphonium ylides(111) involves the breaking of carbon-phosphorus bond yielding a carbonyl compound(112), which further reacts with excess of starting ylide(111) to give an olefin(113) and phosphine oxide$^{111,112}$ (Scheme I.54).

The autoxidation reactions have also been applied to bis ylides(114) resulting in the formation of cyclic olefins, acenaphthylene(115)(Scheme I.55). Similarly, a heterocyclic olefin(117) is obtained by
Scheme I.52

\[ \text{Ph}_3\text{P} = \text{CH}_2 + \text{R} - \text{X} \rightarrow \text{Ph}_3\text{P} - \text{CH}_2 - \text{R} \text{X} \]  

\[ \text{or} \]

\[ \text{base} \]

\[ \text{R} = \text{alkyl, aroyl} \]

\[ \text{Ph}_3\text{P} = \text{CHR} \]

Scheme I.53

\[ \text{R}_3\text{P} - \text{CH} \rightarrow \text{R}_3\text{P} - \text{CH} \text{R}_1 \]

\[ \text{acid} \]

\[ \text{base} \]

\[ \text{HX} \]

\[ \text{HX} \]

Scheme I.54

\[ \text{Ph}_3\text{P} = \text{CRR}_1 + \text{O}_2 \rightarrow \text{RR}_1\text{C}=\text{O} + \text{Ph}_3\text{PO} \]

\[ \text{ac} \]

\[ \text{bas} \]

\[ \text{RR}_1\text{C}=\text{CRR}_1 + \text{Ph}_3\text{PO} \]

Scheme I.55

\[ \text{Ph}_3\text{P} = \text{CH} \rightarrow \text{PPh}_3 \]

\[ \text{O}_2 \rightarrow \]

\[ \text{+ 2Ph}_3\text{PO} \]
Scheme 1.56

\[ \text{Ph}_3\text{P}=\text{C} \equiv \text{CH} \text{PPh}_3 + \text{O}_2 \rightarrow \text{Ph}_3\text{P} - \text{C} \equiv \text{CH} \text{PPh}_3 + 2\text{Ph}_3\text{PO} \]

Scheme 1.57

\[ \text{Ph}_3\text{P}=\text{CH} \text{R}^1 + \text{R} - \text{X} \rightarrow \text{Ph}_3\text{P} - \text{CH} \text{R}^1 \]

\[ \text{Ph}_3\text{P} - \text{CH}_2 \text{R}^1 \text{X} + \text{Ph}_3\text{P}=\text{C} \text{R} \]

Base or ylide (113)

Scheme 1.58

\[ \text{Ph}_3\text{P} - \text{CH} - \text{C} \equiv \text{C}_6\text{H}_5 + \text{H}_5\text{C}_2 \text{O} \rightarrow \text{Ph}_3\text{P} - \text{CH} - \text{C} \equiv \text{C}_6\text{H}_5 + \text{C}_2\text{H}_5\text{I} \]

\[ \text{Ph}_3\text{P} - \text{CH} = \text{C} - \text{C}_6\text{H}_5 + \text{H} \text{OC}_2\text{H}_5 \]

\[ \text{Ph}_3\text{P} - \text{C}=\text{C} - \text{C}_6\text{H}_5 + \text{I} \]
the oxidation of a bis ylide(116)$^{113}$ (Scheme I.56).

The oxidizing agents usually used in the oxidation of ylides are ethyl nitrate$^{114}$ lead tetraacetate, dibenzoyl peroxide, Phenyl iodide diacetone and lead dioxide$^{115}$. The oxidation with Ozone$^{116}$ and periodate$^{117}$ has been found to be specifically useful in the synthesis of dicarbonyl compounds.

B.3.3. Alkylation of Ylides

Phosphonium ylides(118) on alkylation with alkyl halide form phosphonium salts(119), which on further treatment with base or another mole of the starting ylide(118) gave alkylated ylide(120) and precursor (121) of ylides(118)$^{118}$ (Scheme I.57). On the other hand, carbonyl stabilized ylides(122) on reaction with alkyl halide form C-alkylated product(123) and O-alkylated product(124)$^{119}$ (Scheme I.58).

If the ylide contains a halogen in the long chain attached to carbanion portion, intramolecular alkylation may occur to yield cyclic products (125)$^{121-128}$ (Scheme I.59).

B.3.4. Acylation of Ylides

The acylation of ylide(126) with acid chloride yields an acylated phosphonium salt(127) which on treatment with base or a mole of ylide(126) affords a carbonyl stabilized ylide(128)$^{122}$ (Scheme I.60). Acid esters$^{123,124}$, chloroformic acid e-ster$^{122}$, acid
Scheme 1.59

\[
\begin{align*}
\text{CH}_2-\text{CH}_2-\text{Br} & \xrightarrow{\text{Base}} \text{CH}_2-\text{CH}_2-\text{Br} & \text{CH}_2-\text{CH}_2-\text{Br}^\oplus \\
\text{CH}_2-\text{CH}_2-\text{PPh}_3 \text{Br} & \xrightarrow{\text{Base}} \text{CH}_2-\text{CH}-\text{PPh}_3 & \text{CH}_2-\text{CH}-\text{PPh}_3^\oplus \\
\text{CH}_2-\text{CH}_2 & \xrightarrow{\text{PhCH}=\text{O}} \text{CH}_2-\text{CH}_2 & \text{CH}_2-\text{CH}_2 \\
\text{CH}_2-\text{C} & \xrightarrow{\text{-Ph}_3\text{PO}} \equiv \text{CH}-\text{Ph} & \text{CH}_2-\text{C} & \equiv \text{PPh}_3
\end{align*}
\]

Scheme 1.60

\[
\text{Ph}_3\text{P}==\text{CH}-\text{R}^1 + \text{R CO Cl} \rightarrow \left[ \text{Ph}_3\text{P}^{\oplus}==\text{CH}-\text{R}^1 \right]^\ominus
\]

\[
\text{Ph}_3\text{P}^{\oplus}=\text{CH}_2-\text{R}^1 \ominus + \text{Ph}_3\text{P}==\text{C}\backslash\text{O}=\text{C}==\text{R}
\]

Scheme 1.61

\[
2\text{Ph}_3\text{P}==\text{CH}_2 + \text{R}^1-\text{N}=\text{C}\backslash\text{Cl} \rightarrow \text{Ph}_3\text{P}==\text{CH}==\text{C}==\text{N}==\text{R}^1
\]

\[
\text{Ph}_3\text{P}^{\oplus}=\text{CH}_3 \ominus + \text{Ph}_3\text{P}^{\oplus}=\text{CH}_2-\text{Cl}
\]
anhydride\textsuperscript{125}, thiocarbonic acid and 5-ethyl e-
sters\textsuperscript{122} may also be used as acetylationg agents.

The benzoylation of semistabilized phosphonium ylides to yield highly stabilized ylides via transylida-
tion reaction has also been studied by Tewari et al\textsuperscript{126}. Recently, Yoshida et al\textsuperscript{127} have reported the reaction of the ylide(129) with imidoyl chloride(130) to form \(\alpha\)-iminophosphonium methyldienes(131) via transylidation reaction(Scheme I.61).

B.3.4. Reactions of Phosphonium Ylides with multipleBond

3.4.1. Carbon-carbon double bond(Wittig reaction)

The most prominent reaction of phosphonium ylides, which attained considerable importance in the synthetic chemistry(organic) under the name of Wittig reaction involves the condensation of these ylides with carbonyl compounds to form olefins and triphenylphosphine oxide\textsuperscript{73,75}. It appears that during the course of the reaction, betaine type of compounds are formed as inter-
mediates(134a). These intermediates(134a) are formed by the nucleophilic attack of ylidal carbonion(132) on the carbonyl group(133) and their decomposition through a cyclic transition state(134b) yields olefins (135) and phosphine oxide\textsuperscript{73,75,128-30}(Scheme I.62). Thus, this reaction in a two step process and either
of the two steps i.e. (a) betaine formation and (b) its decomposition may be the rate determining step.

Mechanism of Reaction

(a) Betaine formation

The nucleophilic addition of alkylidene phosphorane in its ylide form to a polarised carbonyl compound involves the beta-ine formation (134b). As a consequence of the greater affinity of phosphorous for oxygen and tendency of phosphorus atom to expand the valence shell to 10 electrons, P-O bond is formed next giving rise to the four membered ring compound.

The nature of substituents \( R^1 \) and \( R^2 \) in the carbanion portion as well as of the group \( R \) on phosphorus determine the ease with which the betaine intermediate is formed. It has been observed that electron withdrawing nature of group \( R \) increase the d orbital resonance and thereby favours ylene form, thus decreasing the reactivity of ylide. If, on the other hand, group \( R \) has electron releasing substituents, the magnitude of formal charge on phosphorus atom decreases to make greater contribution towards the ylide form. As a consequence the reactivity of the ylide is increased\(^2,3,6\). The electron withdrawing nature of the groups \( R^1 \) and \( R^2 \) on carbanion side stabilizes the negative charge and, consequently, nucleophilic character of the ylide is diminished. Conversely, the electron releasing nature of \( R^1 \) and \( R^2 \) increase the nucleophilicity of the ylide.
(b) Betaine decomposition

The decomposition of the betaine to olefin\(^{135}\) and phosphine oxide occur by the attack of the oxyanion on the phosphorus atom, forming four membered cyclic betaine\(^{134b}\)\(^{131}\). The driving force for the decomposition of betaine is derived from the formation of P-O bond because of greater affinity of tertiary phosphine for oxygen. This step will be retarded by substituents \(R\) which decrease the positive character and hence oxygen affinity of the phosphine\(^{+I, +M}\) or hyperconjugative effect) and accelerated by the substituents \(R^1\) to \(R^4\) which can conjugate with incipient double bond in transition state. This clearly indicates that the factors which help betaine formation hinder betaine decomposition and vice versa\(^{132-34}\).

Stereochemistry

In a majority of cases, Wittig reaction appears to yield trans olefins as the dominant product\(^{135-40}\). Recent investigations have, however, revealed that normally the carbonyl olefination (Wittig reaction) is not stereoselective and both the isomers are obtained in comparable amounts. Only in some instances, predominant formation of cis or trans olefins has been reported\(^{141}\). Even such cases give rise to questionable mechanistic interpretations. The stimulated research in this area which led to the achievement of ste-ric
control of the olefin synthesis.

On the basis of the mechanism discussed above, if the ylide and carbonyl compound are unsymmetrically substituted, a mixture of cis- and trans- olefins is formed. The ratio of the two forms appears to be governed by a combination of steric factors and reaction conditions\(^2,3,6,142\).

A phosphonium ylide may also react with a carbonyl compound to yield a betaine with either the erythro(136) or threo configuration(137)(Scheme I.63).

As the sterically less hindered betaine has threo configuration, it is to be expected that trans-isomer being thermodynamically more stable would predominate. It has been stated that there is no direct conversion of one betaine into other but only through reversion to the starting ylide and carbonyl compound\(^143\). However, in presence of phenyllithium, the interconversion of the betaines(136 & 137) is extremely rapid with the equilibrium as shown in Scheme I.63. Addition of HCl followed by potassium + butoxide gives pure trans olefins\(^144\). In a non-polar solvent, the trans isomer is the predominant product. However, as the polarity of the solvent is increased the yield of cis-olefin also increases.

The presence of an excess of either reactant and addition of nucleophiles and salts such as LiI tends
to increase the proportion of cis form\textsuperscript{142}. Thus, by proper control of reaction conditions, carbonyl olefination can be made stereoselective to yield a particular isomer, thereby making Wittig reaction a useful tool in the hands of synthetic organic chemists. Thus, stereoselective olefination of carbonyl has been applied in the preparation of naturally occurring fatty acids\textsuperscript{142}.

Applications

Wittig reaction, involving condensation of phosphonium ylides with carbonyl compounds to yield olefins and phosphine oxide, has attained considerable importance in synthetic organic chemistry. The possibility of stereoselective carbonyl olefination to yield the desired isomer has made it a particularly useful reaction involving a variety of synthesis.

Thus, phosphonium ylides have been used in the synthesis of a wide range of natural products such as terpenoids phyto\textsuperscript{145}, \(\beta\)-bisabolens\textsuperscript{146} and lanceol\textsuperscript{147}(Scheme I.64). Synthesis of a number of plant pigments such as \(\beta\)-carotene\textsuperscript{148} and lycopene\textsuperscript{149} has also been carried out. It has also been found useful in the preparation of Vitamin A\textsuperscript{150} and D\textsuperscript{151}. The exten-
Scheme I.62

\[
\begin{align*}
&\text{Ph}_{3}P\text{O} + \text{R}^1\text{R}^2\text{C}=\text{CR}^3\text{R}^4 \\
\text{Ph}_{3}P\text{O}^+ &\xrightarrow{\text{K}_3} \text{Ph}_{3}P\text{O} \quad \text{cis-olefin} \\
\text{R}^1\text{R}^2\text{C}=\text{CR}^3\text{R}^4 &\xrightarrow{\text{K}_6} \text{trans-olefin}
\end{align*}
\]
**Scheme I.65**

\[(H-C-OR)_n + \text{Ph}_3\text{P} = \text{CHCOR}^1 \rightarrow (H-C-OR)_n \]

Phosphorane

Protected or unprotected aldehydo sugars

**Scheme I.66**

**Scheme I.67**

**Scheme I.68**
sion of sugar chain in carbohydrate chemistry\textsuperscript{152-54} (Scheme I.65) has also been brought about by using the reaction. In the recent times, this reaction has been applied in the synthesis of 11-deoxyprostaglandins\textsuperscript{155-56} (Scheme I.66), macrocyclic\textsuperscript{157} (Scheme I.67) and heterocyclic compounds\textsuperscript{158} (Scheme I.68).

3.4.2 Reaction with N=O group

Like the carbonyl group, nitroso compounds also undergo Wittig reaction with phosphonium ylides\textsuperscript{(138)} to form C-N double bond systems\textsuperscript{(139)} which further react with a second mole of the ylide\textsuperscript{(138)} to give an olefin\textsuperscript{(141)} and iminophosphoranes\textsuperscript{(142)}\textsuperscript{159} (Scheme I.69).

3.4.3. Reaction with C=N group

It has been reported that the ylide \textsuperscript{(143)}, which lack B-CH group, react with Schiff's bases\textsuperscript{(144)} to give olefins\textsuperscript{(145)} and iminophosphoranes\textsuperscript{(146)} while the ylides\textsuperscript{(147)} with \textsuperscript{−CH\textsubscript{2}} group undergo a different reaction with benzalniline\textsuperscript{(148)} to give allenes\textsuperscript{(150)} forming betaine intermediates\textsuperscript{(149)} in the course of the reaction\textsuperscript{159} (Scheme I.70).

3.4.4. Reaction with C = N group

Benzyldenetriphenylphosphorane\textsuperscript{(151)} reacts with benzonitrile\textsuperscript{(152)} to give iminophosphorane\textsuperscript{(154)} via the intermediacy of a cyclic product\textsuperscript{(153)}\textsuperscript{160}. The hydrolysis of cyclic product\textsuperscript{(155)} yields ketones\textsuperscript{161} (Scheme I.71).
3.4.5. **Reaction with C-C triple bond**

The phosphonium ylides(156) with acetylenedidecarboxylic acid esters(157) lead either through betaine formation (158) or through direct cycloaddition to the phosphacyclobutane(159) which undergoes ring opening to give a more stable phosphorane\(^{162}\)(160)(Scheme I.72).

**B.3.5. Reaction with 1,3-Dipolar compounds**

3.5.1. **Reaction with azide**

Phenyl azide(161) reacts with benzylidene-triphenylphosphorane(162) to yield benzalaniline(163) and N-phenyltriphenylphosphinimine(164)\(^{163}\)(Scheme I.73).

3.5.2. **Reaction with nitrones**

It has been reported that phosphonium ylides (165) add to nitrones(165) to give new heterocyclic system i.e. 1,2,5 P(V)-oxazaphospholidines(167)\(^{164}\)(Scheme I.74). It has been suggested that the addition is a one step multiple centre process.\(^{165}\)

3.5.3. **Reaction with nitrile oxides**

Phosphonium ylides (168) and nitrile oxide(169) interact to give 4,5-dihydro-1,2,5-P(V)-oxazaphospholenes(170) whose thermal decomposition yields different products depending upon the nature of substituents\(^{166,167}\)\(^{1}\) R, R', R\(^{2}\)(Scheme I.75). Thus, the groups R\(^{1}\) and R\(^{2}\) when associated with -I and -M effects cause the formation of keteneimines(171), while the same groups which possessed electron donating tendency affect the formation
of azirines(172). When R exhibits -I effect and at the same R₁ and R² show +I effect, the products are triphenylphosphine and α,β-unsaturated oxime(173)\(^{166}\).

B.3.6. Reaction of Phosphonium Ylides with Ethers

Recently, Subramanyam et al.\(^{168}\) have studied that the reaction of phosphonium ylides(174) with ethyl formate gave substituted vinyl ethers(175) via the course of Wittig reaction(Scheme I.76) instead of aldehydes as reported by Trippett et al.\(^{169}\). On the other hand, α-iodo or α-bromoacetic acid esters(176) form phosphonium salts(177) using ylides(174) from which by transylidation reaction, a new ylide(178) is produced(Scheme I.77). However, mono, di and trifluoroacetic esters(179) and phosphonium ylide(180) undergo Wittig reaction at the ester carbonyl group which results in the formation of enol ethers(181) of fluoropetones\(^{170}\)(Scheme I.78).

B.3.7. Reaction of ylides with lactones

β-Propiolactone(182) and γ-butyrolactone(183) with alkylidenediarylphosphoranes(184) yield phosphinocarboxylate betaine(185), thermolysis of which give triphenylphosphine and lactones(186) with the alkylidene group of the starting phosphorane(184) introduced in the ring\(^{171}\)(Scheme I.79).

On the other hand, enol lactone(187) with stabilized ylides(188) give normal Wittig products(189-190)\(^{172}\)(Scheme I.80).
Scheme I.75

Ph₃P═CR¹R²

\[ \xrightarrow{168} \]

\[ + \]

\[ \xrightarrow{169} \]

\[ R-C≡N-O^\ominus \]

\[ \xrightarrow{170} \]

\[ R^1C≡N-O^\ominus \]

\[ \xrightarrow{172} \]

\[ R^1C≡N-O \]

\[ \xrightarrow{171} \]

\[ R^1R^2C≡C≡N-R \]

Scheme I.76

Ph₃P

\[ \xrightarrow{174} \]

\[ R-CH + C=OR² \]

\[ \xrightarrow{175} \]

\[ R-CH=C=OR² \]

\[ \xrightarrow{175} + \]

Ph₃PO
Scheme I.77

\[
\text{Ph}_3\text{P} = \text{CHR} + \text{X-CH}_2\text{COOR}^1 \rightarrow \text{R-CH-CH}_2\text{COOR}^1 \oplus \text{PPh}_3
\]

\[
\text{X = Br, I}
\]

\[
\text{ylide} \xrightarrow{(174)} \text{R-CH}_2\text{PPh}_3 \oplus \text{X} + \text{R-C-CH}_2\text{COOR}^1
\]

\[
\text{PPh}_3
\]

Scheme I.78

\[
\text{Ph}_3\text{P} = \text{CH-R} + \text{X-C-OEt} \rightarrow \text{R-CH=C} \xrightarrow{\text{X}} \text{C-OEt} + \text{Ph}_3\text{PO}
\]

\[
\text{X = CH}_2\text{F, CHF}_2, \text{CF}_3
\]

Scheme I.79

\[
\text{(CH}_2\text{)}_n\text{C=O} + \text{Ph}_3\text{P}=\text{CH}_2 \rightarrow \text{(CH}_2\text{)}_n\text{COO}^\ominus \oplus \text{CH}_2\text{PPh}_3
\]

\[
\text{\Delta} \rightarrow \text{(CH}_2\text{)}_n\text{C=O} \oplus \text{Ph}_3\text{P}
\]

\[
\text{n = 2}
\]

\[
\text{n = 3}
\]
B.3.8. Reaction with cyanohydrine

When phosphonium ylide\(^{(191)}\) is reacted with substituted benzaldehydecyanohydrine\(^{(192)}\) in the presence of NaOC(CH\(_3\))\(_3\) to form stilbenes\(^{(193a-b)}\) having E, Z-conformations. The course of reaction is analogous to Wittig reaction\(^{173}\) (Scheme I.81).

B.3.9. Reaction with chalcones

The course of reaction of phosphonium ylides with carbonyl systems is quite different to that of analogous pyridinium ylides. But, the reaction of phosphonium ylides\(^{(194)}\) with \(\alpha,\beta\)-unsaturated ketones\(^{(195)}\) so called chalcones in presence of ammonium acetate undergoes azo ring closure leading to the synthesis of 2,4,6-triarylpuridines\(^{(196)}\)\(^{174}\) analogous to the pyridinium\(^{175-178}\) sulphonium\(^{179}\) and arsonium ylides\(^{180}\) (Scheme I.82).

B.3.10. Reaction with N-sulfinylamine

The reaction stable phosphonium ylides with N-sulfinylamines give different products depending upon the nature of R group attached to nitrogen atom of sulfinylamine\(^{181}\). Thus, when substituted fluorenylidene-triphenylphosphoranes\(^{(198)}\) reacted with N-sulfinyl \(-p\)-toluenesulfonamide\(^{(197a)}\) on S = O bond of (197a) to give S-imide\(^{(199)}\) and phosphine oxide analogous to Wittig reaction. On the other hand, the same ylides\(^{(198)}\) attack on N=S bond of N-sulfinyl p-nitroaniline\(^{(197b)}\)
Scheme 1.81

\[ \text{Ph}_3\text{P}^- \text{CH} - \text{C}_6\text{H}_4 - \text{R}^1 + \text{C}_6\text{H}_5 - \text{CH} - \text{C} = \text{N} \rightarrow \text{(CH}_3)_3\text{C} - \text{ONa} \]

\[ \text{191} \quad \text{192} \]

\[ \text{193a} \quad \text{193b} \]

Scheme 1.82

\[ \text{Ph}_3\text{P}^- \text{CH} - \text{C}_6\text{H}_5 - \text{C} = \text{C} - \text{CHO} \]

\[ \text{194} \]

\[ \text{195} \]

\[ \text{196} \]

\[ \text{EtOOCC} - \text{C}_5\text{H}_4\text{C} = \text{C} - \text{C} = \text{C} - \text{COOEt} \]

\[ \text{188} \quad \text{189} \quad \text{190} \]
Scheme I-83

\[ R-N=S=O \]

197a-b

+ 

\begin{align*}
\text{PPh}_3
\end{align*}

198

\[ \xrightarrow{199} \]

\[ \text{S=N-R} \]

\[ \xrightarrow{200} \]

\[ \text{Ph}_3\text{PO} \]

\[ \xrightarrow{201} \]

\[ \text{R}=\text{CH}_3-\text{-SO}_2- \]

\[ \text{R}=\text{NO}_2-\text{-} \]
to yield sulfines(200) and iminophosphoranes(201)(Scheme I.83).

I.C. Studies on some n Sulfuranes (Sulfur Ylides)

Ylides(1) are zwitterionic compounds in which an anion is covalently bonded to a positively charged heteroatom and are considered as a resonance hybrids of two limiting structures, the ylides form(1a) and the ylene form(1b). One of these, the ylide form(1a) emphasizes the Zwitterionic nature involving an Onium Centre at elements like N, P or As next to a carbanionic function which may atleast partially delocalize into suitable substituents. In these ylene form(1b), on the other hand, a true double bond is postulated between the onium centre and the ylidic carbon, thus reducing or even eliminating the formal charges at these atoms\textsuperscript{182,83}. The applications of modern physical techniques and the results of sophisticated theoretical calculations\textsuperscript{184,85,86} have made it increasingly clear that the ylide form predominates in the ground state. Most of the early investigations successfully used this description for most of their problems of structure and reactivity and for the rationalization of reaction mechanism\textsuperscript{183,187}. Therefore, it is with justification that the term ylide is used now-a-days almost exclusively in the literature.
The reactivity of ylides depends both on the properties of the carbanion and on the possible involvement of the hetero atom. These compounds vary widely in stability depending on the symmetry of the molecule and the extent of \( \pi - d^\pi \) bonding. A quantitative comparison of the stability of ylides formed by different elements have been made using the rates of alkali catalyzed exchange\(^{188}\) of the \( \alpha \)-hydrogen atoms of the corresponding salts. The acidity of salt and hence the stability of the ylide is greatly affected by the change in structure.

Ylides have been classified in two main groups, on the basis of stability and the ease with which they undergo reactions with a variety of electrophilic substrates. The first and the larger group comprises the ylide, so called non-stabilized ylide which are generated in the solution from their corresponding salts but could not be isolated due to lack of stabilizing factors and undergo reaction in situ. These ylides may further be divided into two categories depending on the attachment of alkyl or arylalkyl groups with the heteroatom. The arylalkyldene ylides some times designated as semi-stabilized ylides which could not be isolated but persisted in solution for a considerable time, in contrast to the alkylidene ylides which are very short lived. The second and smaller group consists of stabilized
ylides which can be isolated, purified, usually stored in atmosphere and used in subsequent reaction. The stability of them ylides is attributed to the attachment of the electron withdrawing groups with ylidic carbon anion.

In the recent years, synthetic potentialities of ylides have been realized and the studies on these reactive intermediate have been expanded in many directions which led to the exploration of the ylides of N, P, As and S as evidenced by the research monographs\textsuperscript{182,183,189-193} and comprehensive review articles\textsuperscript{194-204}.

The involvement of a particular heteroatom results in remarked differences in the chemical and physical behaviour of different types of ylides. A separate description on many aspects of the chemistry of sulfur ylides has been explored in the present programme.

\textbf{n Sulfurance (S-ylide)}

The chemistry of S-ylide owes its origin from the earliest investigations by Ingold and Tessol\textsuperscript{205} in as early as 1930 when they successfully isolated a stabilized $\pi$-sulfurane –9-fluorenylidene dimethyl sulfuran (203) by reacting 9-fluorenyl dimethyl sulfonium bromide(202) with aqueous $\text{Na}_2\text{CO}_3$(Scheme I.84). But this appeared to be an isolated event because nothing could be added to the literature in regard to the reactivity and synthetic potentialities of this class of compounds.
Schemes

$1a$ (where $X$ may be $N$, $P$, $As$, $S$ etc.)

Scheme 1.84

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{PhCHO} \\
\text{S}^- & \quad \text{CHO}^+ \\
\text{Ph} & \quad \text{Me}_2\text{SO} \\
\text{H}_3\text{C} & \quad \text{CHPh} \\
\text{S}^- & \quad \text{Me}_2\text{SO} \\
\text{Ph} & \quad \text{CHOH} \\
\text{H}_3\text{CSH}_2\text{C} & \quad \text{Ph} \\
\text{202} & \quad \text{204} \\
\text{205} & \quad \text{206} \\
\text{207} & \quad \text{208} \\
\text{209} & \quad \text{212}
\end{align*}
\]

Scheme 1.85

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{C} = \text{O} \\
\text{H}_3\text{C} & \quad \text{R} \quad \text{R}' \quad \text{C} = \text{O} \\
\text{H}_5\text{C}_6 & \quad \text{CH}_2 \\
\text{H}_5\text{C}_6 & \quad \text{CH}_2 \\
\text{210} & \quad \text{211} \\
\text{212} & \quad \text{212}
\end{align*}
\]
As a matter of fact, a flurry of activities started in the early sixties\textsuperscript{187,206} when Wittig successfully isolated and studied the reactivity of P-ylides towards carbonyl compounds. However concluding from the fact that any molecular system capable of providing adequate stabilization to a carbanion may form an ylide\textsuperscript{207}, system and prompted from Wittig investigations in the P-ylide chemistry, Johnson and Lacount\textsuperscript{208} revived an active interest by successfully isolating fluorenylidene dimenty sulfurane(203). They too could not study the reactivity of this ylide(203) owing to the fact that the ylide afforded sufficient stabilization due to delocalization of the ion pair of electrons present on the ylidic carbanion as represented by resonating forms(3a, b, c) and therefore prevented the ylide\textsuperscript{203} from being entered into reaction with electrophilic substrate. However, their attempts to react the ylide(203) with benzaldehyde to form 9-benzalfluorene (204) failed when benzalfluorene oxide(205) and phenyl-9-(1-Methylthiomyethyl) fluorenly carbinols (206) were formed instead of benzal fluorene (Scheme I.85). Subsequently Corey & Chayleovasky\textsuperscript{209} reported the preparation and reactions of a less stable and more reactive ylide methylene dimethyl oxosulfonium ylide(207). Prompted from the ability of
P-ylide to act as a good carbonyl olefinating reagent.\textsuperscript{187} Corey et al.\textsuperscript{210} have also carried out the reaction of oxosulfonium ylide(207) with aldehyde, Ketones(208) but instead of obtaining olefin-s as was anticipated, epoxides(209) were found to be the exclusive products (Scheme 1.86). These observations accorded oxosulfonium ylides a status of versatile epoxidation reagents and as a result tremendous activities started in this area to explore the synthetic potentialities of these ylides. Soon after Franzen and Driessen\textsuperscript{211} made a successful attempt to synthesize a new class of \( \pi \) sulfursances so called sulfonium ylide(212). Through the interaction of Methylpnenyl sulfide(210) with Methyl iodide(211) followed by dehydrohalogenation(Scheme 1.87). However the ylide(212) so formed was shown to be less stable as compared to oxosulfonium ylide(207). This has been demonstrated by the fact that the ylide gets decomposed in the absence of appropriate substrate.

In the subsequent years Correy & Chaykovsky\textsuperscript{212} have demonstrated that the sulfonium ylides under go not only methylene transfer reaction on carbonyl group to form epoxides but also add on C-C, having some unsaturated group in conjugation to form cyclopropanes. So while methylene dimethyl sulfuranne has distinguished itself as good epoxidation reagent to give oxirane(213) oxosulfolonium methylide has potential to add on the acti-
vated C=C to form cyclopropanes(214). Thus establishing beyond any doubt that π sulfuranes are the best methylene transfer agents(Scheme I.88)\textsuperscript{182,189,213}. In the preceding years, the synthetic potentialities of π-sulfuranes have further been realized and expanded in many directions with a view to test the domain of the applicability of these ylide systems as evidenced by recent monographs and several comprehensive review articles\textsuperscript{214-220}.

A variety of classes of π-sulfuranes are known, the most common being sulfonium ylide(215) oxosulfonium (216), sulfonyl ylides(217), sulfinyl ylides(218) and imminosulfuranes(219).

The stability of π-sulfuranes may be attributed to the electrostatic stabilization as well as delocalization of charge on the carbon ylide with d-orbitals of S-atom\textsuperscript{221,222}. The degree of electrostatic stabilization of π-sulfurane is solely controlled by the magnitude of charges present on theonium group as well as on the carbonyl ylide. This fact can be illustrated by the observations that oxosulfonium ylides are more stable than their sulfonium counter parts, owing to the enhanced positive charge on the S-atom due to the presence of more electronegative oxygen atom. The second factor which also makes a notable contribution to the stability of π-sulfuranes(220) is delocalization involving the
use of 3d-orbitals which is the maximum if the α-sulfur atom carries a full unit of +ve charge. The overlapping of doubly occupied 2p-orbital of the ylide carbon with the unoccupied 3d-orbital of the S-atom takes place resulting in the formation of π-bond while the lone pair on S-remains in a 3p-orbital. This can be represented by the resonance hybrid of two limiting structures, the ylide form(220a) and the ylene form(220b). These factors clearly explain as to why a series of π-sulfuranes have been isolated and characterized as stable species. Further, the maximum overlap of a 2p-carbon orbital(221a) with a 3d orbital of S-atom is reported only when the molecule had tendency to become coplaner(221b) and can be represented by a π-α orbital overlap structure(221).

However, from recent ESCA data, it has been established that the stability of these ylides is also influenced by the presence of certain electronegative groups on the ylide carbon. The reason is that the formal -ve charge on the ylide carbon actually highly delocalized into substituents attached to ylide carbon(222).

The reactivity of π-sulfuranes depends on the properties of the carbanion as well as the possible involvement of the heteroatom212,223-232. Usually the alkylidene sulfuranes of less stability show high reactivity, where as highly stabilized alkylidene sulfuranes
show less reactivity. The reactivity of alkylidene suflurane is influenced by the distribution of the -ve charge over the molecule which, in furan, depends on the nature of the substituents $\text{R}^1$ and $\text{R}^2$ in the alkylidene position as well as on the group $\text{R}$ on sulfur. Thus, the nucleophilic character of the sulfurane decreases while the stability increases if the lone pair of electrons on the $\alpha$-carbon atom of the furan(220a) is delocalized into group $\text{R}^1$ and $\text{R}^2$. The electron with drawing group $\text{R}^1$ and $\text{R}^2$ tend to stabilize the -ve charge and consequently reduce the reactivity of the ylide.

On the other hand, when there is no such interaction, an extremely reactive and unstable ylide is formed.

Prompted from enhanced reactivity, higher stability and easy preparation of the $\pi$-sulfuranes, it was to be thought of interest to focus our attention on synthesizing some new sulfonium ylides with a view to test their reactivity towards a variety of electrophilic substrates, resulting into the formation of diverse carbocyclic and heterocyclic systems.

I.C.1. Preparation of Sulfonium ylides

C.1.1. Ylides from Sulfonium Salts

This is the most common method\textsuperscript{182,237-245} of generating sulfonium ylides and involves the reaction of sulfonium salt with a base which is strong
enough to abstract a proton from the α-Carbon. In principle, any sulfonium salt(223) carrying at least one α-hydrogen is convertible into an ylide(224)(Scheme I.89). In practice the salt method is applicable only in three structural situations. In the first instance all the three of the groups attached to the S-atom must be identical so that it makes no difference which α-hydrogen's removed by the base. In the second instance one or the two of the substituents have no α-hydrogen but those groups which do, are identical. The third and the last structural situation in which the sulfonium salt method is applicable necessitates there being an appreciable difference in the acidity of the various available α-hydorgens and the availability of a base of the proper strength. The deprotonation of the more acidic α-hydrogen is always preferred. If the sulfonium salt(225) possesses three different kinds of α-hydorgens and each of approximately the same acidity, then a mixture of sulfonium ylides 226, 227, 228, results(Scheme I.90).

Numerous bases have been employed for the generation of sulfonium ylides and the strength of base to be used depends on the acidity of the sulfonium salts. Thus trialkyl sulfonium salts required very strong bases such as methyl Lithium, potassium t. butoxide in dimethylsulfoxide or methyle sulphinyl Carbanion.
Further literature survey revealed that in the generation of stabilized ylides only relatively weak bases such as triethylamine, aq. NH$_3$ or aq. NaOH$^{236}$ are respectively required. Also solvents such as dimethyl sulfoxide or tetrahydrofuran are reported to be used for the non-stabilized sulfonium ylides. Protic organic solvents or water have been shown to react with the non-stabilized sulfonium ylides and therefore these solvents have not been employed for their generation.

C.1.2. Ylides from Benzyene and Organic Sulfoxides

Among few other methods employed for the generation of sulfonium ylides, are involving the reaction of dialkyl sulfide(229) with Benzyene(230) is used for the generation of such ylides(231) in which S-atom of the ylide carries one phenyl ring$^{245}$. But in practice, this method is of little importance because the presence of phenyl ring in resulting ylide, reveals them less reactive due to delocalization of +ve charge carried by S-over phenyl ring (Scheme I.91).

C.1.3. Ylides from Alkylation and Acylation Method

A wide variety of complex ylides, which are quite inaccessible by the conventional salt method, have been prepared by the method so called alkylation$^{246}$ or acylation$^{247}$. The method involves the interaction of the simple ylides with alkylating or acylating reagents to form more substituted and stabilized ylides(Scheme I.92).
C.1.4 Ylides from Active Methylene compounds and Sulfoxide

The condensation of active methylene groups(233) with sulfoxides or alkoxy sulfonium salt(232) offers a direct route for the synthesis of highly stabilized ylide(234) via intermediate salt formation$^{248-250}$ (Scheme I.93).

The reaction with sulfoxides is favoured in presence of dehydrating agents. In general, acetic anhydride, phosphorous pent-oxide, Phenyl isocyanate and dicyclohexyl carbodi-imide phosphoric acid are highly suitable for bringing about the desired results.

C.1.5 Ylides from Carbenes

The addition of carbene to a sulfide provides the most direct synthesis of S-ylides(Scheme I.94)$^{251-253}$. Diazocompounds serve as the good source of carbene intermediate for the preparation of ylides(237). The copper catalysed thermal or photolytic decomposition of diazo compounds(236) in the presence of an allyl or benzyl sulfide(235) appears to be the most attractive synthetic technique(Scheme I.95). However, it was also observed that thermal decomposition of diazo compounds is more suitable for synthesizing ylides.

C.1.6 Ylides via Michael addition to a Vinyl sulfonium Salt

The Michael addition to a vinyl sulfonium
salt(238) also produces sulfonium ylides$^{254,255}$ (Scheme I.96). The resulting ylide(239) if stable is isolable and can be trapped by the attack of suitable reagents or it can further react intramolecularly.

C.1.7. Ylides from Electrochemical Reduction of Sulfonium Salt

Only one example relating to the preparation of ylide(241) by this method is given in the literature$^{256}$, which involves the reduction of trimethylsulfonium salt(240) in DMSO solution (Scheme I.97).

C.1.8. Ylides from other methods

Dimethyl sulfonium methyldiene is capable of being prepared in good yields by the phase transfer catalysis$^{257}$. A ligand exchange reaction between triphenyl sulfonium cation and cyclopropyl lithium gives diphenyl sulfonium Cyclopropylide$^{258}$ in high yields. The synthesis of Thiranes$^{259}$ and an assymmetric synthesis of Thoranes$^{260}$ by the reaction of aldehydes and ketones with S-lithiomethyl-o-(-)methyl dithio carbonate have been reported recently.

I.C.2. Reactions of Sulfonium ylides

C.2.1. With halogen acids

Ratis et al$^{236}$ have reported that phenacylidene dimethyl sulfonium ylide on its reactions with HBr acid affords dimethyl phenacyl sulfonium bromide. Johnson et al$^{247}$ tested the reaction and demonstrated that almost
all the carbonyl stabilized sulfonium ylides(242) react
with HBr acid(243) to form conjugate acid(244) of the
ylide(242)(Scheme I.98). These observations clearly indi-
cate that sulfonium ylides are nothing but the conjugate
bases of dimethylphenacyl sulfonium bromide.

C.2.2. Thermolysis

The existing literature lacks informations con-
cerning the thermolysis of sulfonium ylides. However
Johnson et al.\textsuperscript{234} have shown that the non-stabilized sul-
fonium ylide, diphenyl sulfonium benzylide(245), on ther-
molysis dissociates into carbenes(246) and phenylsulfide
(247)(Scheme I.99). Contrary, thermolysis of stabilized
ylide, phenacylidene dimethyl sulfurane(248), takes diffe-
rent course\textsuperscript{261,262} where carbene generated by the thermal
dissociation of the ylide dimerises to form dibenzoyl
ethylene which in turn\textsuperscript{\textsuperscript{15}} attacked by one mole of the origi-
nal ylide(248) affording 1,2,3 tribenzoyl cyclopropane
(249) through carbenoid mechanism(Scheme I.100).

C.2.3. Photolysis

Photolytic conversions of the sulfonium ylides
have been less studied. However, Trost\textsuperscript{263} has reported
that photochemical decomposition of diphenyl sulfonium
allylide(250)occurs in which cyclopropane(251) is isolated
in 25% yield.(Scheme I.101). Subsequent to this, Corey
and Chaykasky\textsuperscript{264} developed in Arnö-Eistert type of pro-
cess, of yielding esters(254) by irradiation of 3-keto-
Scheme 1.95

\[ R = C + \text{CH}_3\text{OOCCN}_2 \quad \text{hv} \quad \text{or} \quad \Delta / \text{Cu} \quad \text{CH}_3\text{OOCC} = \text{COCH}_3 \]

235 \quad 236 \quad 237

Scheme 1.96

\[ \text{CH}_2=\text{CH} - \text{CH} = \text{CHS}^+ (\text{CH}_3)_2 + \text{NaOCH}_3 \rightarrow \text{CH}_3\text{OCH}_2\text{CH} = \text{CHC} = \text{CHS}^+ (\text{CH}_3)_2 \]

238 \quad 239

Scheme 1.97

\[ (\text{CH}_3)_3^+ S \quad \overset{\varepsilon}{\text{DMSO}} \rightarrow (\text{CH}_3)_3^+ S \quad \overset{-H}{\rightarrow} \quad (\text{CH}_3)_2^+ S - \text{CH}_2 \]

240 \quad 241

Scheme 1.98

\[ (\text{CH}_3)_2 S = \text{CH} - \text{C} = \text{Ar} + \text{HBr} \rightarrow (\text{CH}_3)_2 S - \text{CH}_2 - \text{C} = \text{Ar} \quad \overset{\text{Br}^+}{\text{O}} \]

242 \quad 243 \quad 244

Scheme 1.99

\[ (\text{C}_6\text{H}_5)_2^+ S - \text{CHC}_6\text{H}_5 \quad \overset{\Delta}{\rightarrow} \quad \text{CHC}_6\text{H}_5 + (\text{C}_6\text{H}_5)_2^+ S \]

245 \quad 246 \quad 247

Scheme 1.100

\[ (\text{CH}_3)_2 S - \text{CH} - \text{C} = \text{C}_6\text{H}_5 \quad \overset{\Delta}{\rightarrow} \quad [\text{C}_6\text{H}_5 - \text{COCH} = \text{CH} - \text{COC}_6\text{H}_5] \quad \text{C}_6\text{H}_5 \text{COCH} - S\text{Me}_2 \]

248 \quad 249

Scheme 1.101

\[ (\text{C}_6\text{H}_5)_2^+ S - \text{CH} - \text{CH} = \text{CH}_2 \quad \text{hv} \rightarrow \quad \text{H}_5\text{C}_6 \quad + \quad \text{H}_5\text{C}_6 \text{S} \]

250 \quad 251
oxosulfonium ylide(283), prepared by acylation of the methyldiene(252)(Scheme I.102).

C.2.4. With α-Bromo ketones

Johnson et al\textsuperscript{265} have reported that the phenacylidene dimethyl sulfurane(255) reacts either with its conjugated acid(256) or phenacyl bromide(257) to afford tribenzoylcyclopropane(258). The mechanism of the reaction appears to involve an alkylation elimination addition sequence(Scheme I.103).

C.2.5. Alkylation

The alkylation reactions have assumed important because their ability to offer a versatile route for the synthesis of disubstituted ylides which are otherwise difficult to be prepared. Johnson et al\textsuperscript{247} studied the alkylation of phenacylidene dimethyl sulfurane(259) with benzyl bromide(260) where α-methylthio-3-phenyl propiophenone(261) was reported to have been formed(Scheme I.104).

C.2.6. Acylation

Based an information gathered so far non stabilized sulfonium ylides are not liable to be attacked by acylating reagents. However, stabilized sulfonium ylides were reported to undergo acylation reaction with a couple of acylating reagents\textsuperscript{247,266} and it was observed that the course of acylation depends on the nature of the acylating agents. Thus phenacylidene dimethyl
sulfurane(262) on its reaction with benzoic anhydride undergoes C-alkylation to afford a new ylide(263). On the other hand ylide(262) follows O-acylation, when treated with benzoyl chloride, thus affording enol benzoate(264)(Scheme I.105).

C.2.7. With amino compounds

Bravo and his coworkers\textsuperscript{267} have synthesized a variety of substituted indoles(267) by the reaction of dimethyl sulfonium methyldene(265) with aromatic O-amino carbonyl compounds(266)(Scheme I.106). More recently Junjappa\textsuperscript{214} reported the formation of 2-substituted indoles(270) by the interactions of stabilized ylide, phenacylidene dimethyl sulfurane(268) and substituted anilines(269) in the presence of diethylaniline(Scheme I.107).

C.2.8. With Mercapto compounds

Very recently, Bravo et al\textsuperscript{268} have demonstrated that dimethyl sulfonium methyldene(272) is capable of undergoing reaction with O-mercapto ketones(271) forming substituted benzo Thiophanes(273)(Scheme I.108).

C.2.9. With Nitrile Imine

The carbonyl stabilized sulfonium ylides have also been reported in literature\textsuperscript{269} to undergo reaction with nitrile imines affording pyrazole derivatives. For example, the reaction of stabilized sulfurane(274) with \textit{N}-(\textit{\textgreek{a}}-Chloro benzylidene)\textit{N}-phenyl hydrazine(275) affords
pyrazole(277) via intermediacy of the cyclic product(276). This reaction assumed much importance in the synthesis of pyrazole derivatives(Scheme I.109).

C.2.10 With Multiple Bonds

C.2.10(i) With C=O Double Bond

The best known reaction of sulfonium ylides\(^{189}\) which attained importance in the preparative organic chemistry under the name of epoxidation involves the condensation of these ylides(278) with corbonyl compounds (279) to form oxiranes(281) exclusively. The reaction appears to proceed via the intermediacy of betaine type of compound(280), formed by the nucleophilic attack of the ylidic carbanion on the carbonyl carbon atom and involving displacement by the oxyanion on the carbon carrying the onium group. It appears\(^{270}\) in the case of sulfonium betaine(280) that the potential S-O bond formation is not sufficient driving force to dictate the course of the reaction(Scheme I.110). The conjugation and stabilization afforded by the substituents(R) present on the ylide as well as on the carbonyl group (R\(^2\) & R\(^3\)) to an incipient double bond in the transition state appears to be the rate controlling factor. In the absence of such stabilization, oxirane's formation may very easily be the normal course of events as is observed in the case of Methylides\(^{271}\).

Non stabilized sulfonium ylides e.g. methylene dimethyl sulfurane(282) when reacted with carbonyl
compound(283) such as benzaldehyde cyclohexanone and benzophenone, afforded the epoxides(284) in fair to good yields(Scheme I.111). In the year 1961 Frazen et al\textsuperscript{235} further extended the reactions of these ylides with $\alpha,\beta$-unsaturated ketones and have shown that the methylene transfer reaction takes places at C=O bond and not at C=O bonds, as evidenced by the formation of epoxides and non-isolability of cyclopropanes.

In the subsequent years, Johnson et al\textsuperscript{239,272} took the credit of synthesizing substituted benzyldiene phenyl sulfurane(285) and have studied their reactions with carbonyl compounds(286) which led to the formation of epoxide(287) exclusively(Scheme I.112).These studies revealed that in $\gamma$-sulfuranes unlike arsonium ylides\textsuperscript{273} the course of the reaction with carbonyl compounds can not be affected by the nature of the group present on the benzylic position of the ylide carbanion. As a result, these ylides\textsuperscript{274} have been successfully employed for the synthesis of nitrosubstituted stilbenes oxide which are quite inaccessible by their arsonium counter parts owing to the fact that nitro group tends the reaction to proceed in the direction of olefins formation.

Unlike non-stabilized sulfonium ylides which are quite reactive against carbonyl functions giving epoxides exclusively stabilized sulfonium ylides\textsuperscript{241} do not react with carbonyl functions. Non-reactivity towards carbonyl function is due to the decrease nucleophilicity
Scheme 1.110

\[
\begin{align*}
S^+ \text{C}_R^1 & + \text{C}^\equiv \text{C}^O \rightarrow \\
& \text{S}^+ \text{C}_R^1 \\
\end{align*}
\]

Scheme 1.111

\[
\begin{align*}
\text{H}_3\text{C}^+ \text{O} \rightarrow \text{H}_3\text{C}^+ \text{O} \\
\text{R}^1 & + \text{C}^O \rightarrow \text{R}^1 \text{C}^O \\
& \text{C}^O \text{CH}_2 + (\text{CH}_3)_2 \text{S} \\
\end{align*}
\]

Scheme 1.112

\[
\begin{align*}
(\text{C}_6\text{H}_5)_2\text{S}+\text{CH}-\text{C}_6\text{H}_5 & + \text{C}_6\text{H}_5\text{CHO} \rightarrow \text{H}_5\text{C}_6\text{HC} \text{C}_6\text{H}_5 \\
& + (\text{C}_6\text{H}_5)_2\text{S} \\
\end{align*}
\]

Scheme 1.113

\[
\begin{align*}
\text{Naphthalene}^+ \text{(CH}_3)_2 \text{S} & + \text{PhCHO} \rightarrow \text{Naphthalene}^+ \text{(CH}_3)_2 \text{S} \\
(\text{CH}_3)_2 \text{S} & + \text{Naphthalene} \rightarrow \text{Naphthalene}^+ \text{(CH}_3)_2 \text{S} \\
\end{align*}
\]

Scheme 1.114

\[
\begin{align*}
(\text{CH}_3)_2\text{S}+\text{CH}_2 & + \text{C}_6\text{H}_5\text{CH=CH}-\text{C}_6\text{H}_5 \rightarrow \text{C}_6\text{H}_5\text{CH=CH}-\text{C}_6\text{H}_5 \\
& + (\text{CH}_3)_2 \text{SO} \\
\end{align*}
\]
of these ylides. However Johnson and Ler Count\textsuperscript{208} were first to study the reaction between stabilized sulfonium ylide, fluorenylidene dimethyl sulfurane(288) and benzaldehyde(289) where epoxide(290) was found to be the exclusive product(Scheme I.113). There after Payne et al\textsuperscript{275} have demonstrated that stabilized ylides could be made to react carbonyl group is in conjugation with the highly electropositive group which enhances the electrophilic character of carbonyl carbon atom, thus making them to enter into reaction with the sulfonium ylides.

C.2.10.(ii) With C-C Double Bond

Prompted from the ability of sulfonium ylides\textsuperscript{189} to act as a versatile methylene transfer reagent as evidenced by the fact that they form epoxides on their attack on carbonyl function, curiously aroused among the organic chemists to explore the reactivity of sulfonium ylides towards C=C. One of the first examples in this direction came from the investigations carried out by Corey & Chaykovsky\textsuperscript{209,212} which involved the nucleophilic addition of dimethyl oxosulfonium methyldide(291) with Chalcone(292) to produce trans-1-benzoyl-2-phenyl cyclopropane(293)(Scheme I.104). However cyclopropanation reactions starting from sulfonium salts(294) to form 1,2,3 tribenzoylcyclopropane(297) were also known earlier\textsuperscript{276} although mechanism of the reaction was not clear. Only in 1966 it was demonstrated\textsuperscript{261,262} that the
reactions proceeded by the addition of dimethyl sulfoxonium phenacylide(95) to dibenzoyl ethylene(296)(Scheme I.115). However, the ease with which cyclopropanation takes place depends on the nucleophilic character of the ylide carbamion. This can be illustrated by the fact that non-stabilized sulfoxonium ylides readily attack over C=C bond, due to enhanced nucleophilicity by the absence of stabilization factors giving cyclopropane derivatives. On the other hand it was observed that stabilized sulfoxonium ylides which are relatively less nucleophilic, attack on conjugated C=C systems only.

Subsequent to these investigations, the method introducing cyclopropane has become one of the most widely utilized methods besides are involving carbene addition. Payne\textsuperscript{277} has shown by studying the addition of carbethoxy dimethyl sulfoxonium ylide(298) to the hexenone(299) that the nucleophilic methylene transfer takes place at the α,β-double bond to form cyclopropane(300) and not on carbonyl group(Scheme I.116). In this way cyclopropanated steriods\textsuperscript{278} and nucleosides\textsuperscript{279} have been synthesized.

C.2.10(iii) With C-N Double Bond

Franzen\textsuperscript{211} and Corey\textsuperscript{212} have studied the reaction of non-stabilized sulfoxonium ylide, methylene dimethyl sulforane(301), with schiff's bases(302), leading to the formation of a variety of aziridines(303) (Scheme I.117). Hoffmann et al\textsuperscript{281} have demonstrated that
the same ylide (301) can also affect other C-N double bond systems when he synthesized 1-azabicyclobutanes (305) by the direct condensation of the ylide (301) with aziridines (304) (Scheme I.118).

However, the stabilized sulfonium ylides differ from the non-stabilized sulfonium ylides in so far as their course of reaction with schiff's bases is concerned and it was observed \(^{243}\) that unlike non-stabilized sulfonium ylides, stabilized ylides (306) on their reaction with schiff's bases (307) produce arylaminocinnamaldis (308) and not aziridines (Scheme I.119).

C.2.10(iv) With C-S Double Bond

Corey and Chaykovsky \(^{212}\) have reported that the methylene dimethyl sulfurane (307) on its reaction with benzothiophenone (310) affects the methylene transfer at C=S bond affording the thio oxirane (311). The reaction follows the same course as with benzophenone (Scheme I.120).

C.2.10(v) With N-O Double Bond

The reaction of the nitroso compounds with sulfonium ylides leads to the synthesis of C-N double bond. Johnson \(^{233}\) demonstrated that it was fairly an addition elimination methylene transfer reaction of sulfonium ylide which produces oxime. Thus fluorenylidene dimethyl sulfuranene (312) and nitrosobenzene (313) were shown to undergo an exothermic rapid reaction to afford the nitrone
\[
(\text{CH}_3)_2S\cdot\text{CH}_2\cdot\text{C}\cdot\text{C}_6\text{H}_5 \quad \xrightarrow{294} \quad \begin{array}{c}
\text{H}_5\text{C}_6\text{OC}
\end{array}
\]

\[
(\text{CH}_3)_2S\cdot\text{CH}\cdot\text{C}\cdot\text{C}_6\text{H}_5 \quad \xrightarrow{295} \quad \begin{array}{c}
\text{C}_6\text{H}_5\cdot\text{COCH}='\text{CHCO}_6\text{H}_5
\end{array}
\]

\[
\text{Scheme 1.116}
\]

\[
(\text{CH}_3)_2S\cdot\text{CHCOOC}_2\text{H}_5 \quad + \quad \text{C}_6\text{H}_6 \quad \xrightarrow{298, 299} \quad \begin{array}{c}
\text{COOC}_6\text{H}_5
\end{array}
\]

\[
\text{Scheme 1.117}
\]

\[
(\text{CH}_3)_2S\cdot\text{CH}_2 \quad + \quad \text{C}_6\text{H}_5\cdot\text{CH}='\text{NC}_6\text{H}_5 \quad \xrightarrow{301, 302} \quad \begin{array}{c}
\text{C}_6\text{H}_5\cdot\text{CH}='\text{N}='\text{C}_6\text{H}_5 \\
\quad + \quad (\text{CH}_3)_2\text{S}
\end{array}
\]

\[
\text{Scheme 1.118}
\]

\[
(\text{CH}_3)_2S\cdot\text{CH}_2 \quad + \quad \begin{array}{c}
\text{Ph}
\end{array} \quad \xrightarrow{301, 304} \quad \begin{array}{c}
\text{R}
\end{array}
\]

\[
\text{Scheme 1.119}
\]

\[
(\text{CH}_3)_2S\cdot\text{CH}='\text{C}='\text{R} \quad + \quad \text{ArCH}='\text{NAr}' \quad \xrightarrow{306, 307} \quad \begin{array}{c}
\text{Ar}'\cdot\text{NH} \quad \text{Ar}='\text{C}='\text{CH}='\text{C}='\text{R}
\end{array}
\]

\[
\text{Scheme 1.120}
\]

\[
(\text{CH}_3)_2S\cdot\text{CH}_2 \quad + \quad \begin{array}{c}
\text{H}_5\text{C}_6\cdot\text{C}='\text{S}
\end{array} \quad \xrightarrow{309, 310} \quad \begin{array}{c}
\text{CH}_2 \quad + \quad (\text{CH}_3)_2\text{S}
\end{array}
\]

\[
\text{Scheme 1.121}
\]
N-phenyl fluorenone ketoxime(314)(Scheme I.121)

C.2.11. Metallation

The metallation reactions of sulfonium ylides could not be explored until recently. Only preliminary studies on the reactions of inorganic compounds with the ylides are reported.\textsuperscript{215}

However, it has been shown that the sulfonium ylides(315) being co-ordinatively unsaturated 1,2 dipolar complex of carbon serve as a good ligand for transitional metals(316) in various oxidation states and yield the markedly stable metal complexes(317) of sulfonium ylides(315)(Scheme I.122).

C.2.12. α-Elimination

Evidence for the α-elimination is meagre\textsuperscript{282}. However dimethyl phenacyl ylide(318) has been reported to add an cyclohexene(319) in the presence of sulfate through α-elimination, giving cyclopropane derivative(320) in low yields.\textsuperscript{261} (Scheme I.123). This reaction proceeds via the intermediacy of a copper complexed carbenes to form cyclopropane(320).\textsuperscript{283} Other claims of α-elimination remain even more speculative.

C.2.13 Rearrangements

As revealed by the literature sulfonium ylides have been involved in several types of rearrangements. Thomson and Stevens\textsuperscript{284} have reported that benzyl methyl-phenacyl sulfonium bromide(321) undergoes Stevens rearrange-
ments via the intermediacy of phenacylidone benzylmethyl sulfurane(322) to yield the rearrangement product(323) (Scheme I.124). Houser et al. have demonstrated that the benzylidimethyl sulfonium ion(324) in the presence of amide ion, undergoes sommetel rearrangement to afford the rearrangement product o-methylbenzyl methyl sulfide (325) (Scheme I.125).

In recent years, these rearrangements have been proved to be of great synthetic importance particularly in the synthesis of natural products.251,286
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