SYNTHESIS AND REACTIONS OF TRIPHENYLPHOSPHINE-O-BENZOPHENONIMINE AND DERIVATIVES

A Thesis submitted by

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بسم الله الرحمن الرحيم

"Chemistry creates its subject. This creative ability, similar to that of arts, essentially distinguishes chemistry among the natural science"

Marcelin Berthelot "one of the great organic chemists of the last century"

"Chemistry has strongly creative potential. It can creates substance and material never dreamt of before"

Jack E. Baldwin "one of the great organic chemists of the this century"

Dedication

- To the Memory of my dear friend Omima Ghorashi
- To my parents and all whom I love

Acknowledgements

All praise is due to "ALLA".

I would like to express my deep indebtedness to my supervisor Dr. Farouk Eltayeb for his keen guidance, assistance and continuous encouragement especially pleasant by his fatherly advice and persistent interest and patience made it possible to develop and improve this thesis.

Thanks and deepest gratitude to Dr. Osman Ibrahim, the head Department of Chemistry for his helps.

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My deepest gratitude is also extended to all my friends and colleagues for their good help.

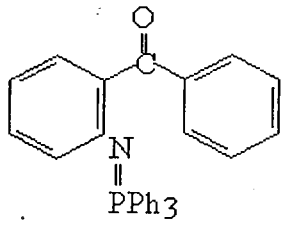
Abstract

o-Aminobenzophenone and its para and meta isomers were prepared using Friedl-Craft benzoylation. Their azides were also prepared via their diazonium salts. The azide of o-aminobenzophenone in its reduced form (o-benzylaniline) and its cyclic ketal were synthesised. All azides thus formed were reacted separately with triphenylphosphine to give the corresponding phopsphinimines, the Wittig reagents nitrogen analoug.

The reactivity of the phosphorous-nitrogen bond. (P $\rightleftharpoons$ N) in the different phosphoranes were studied by two types of reactions.

(1) The Wittig type of reaction using benzaldehyde and its nitro derivatives with each of the above prepared phosphinimines.
While triphenylphosphin-m-benzophenonimine (ii) and the triphenylphosphine benzophenonimine ethylene acetal (v) and it's reduced form triphenylphosphine-o-benzylphenylimine (iv) react giving the corresponding schiffis bases. However, the ortho (i) and the para (iii) isomers failed to react. This lack of reactivity is presumably due to their great stability which came about through the extensive resonance that reduced the nucleophilicity of the nitrogen nucleophile

(2) The phosphinimines each was irradiated using Hanovia medium pressure UV lamp. Also the ortho and para isomers were not affected while others reacted giving the corresponding azo-compound and triphenylphosphine. They were separated and detected by chromatography.



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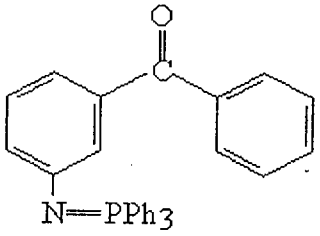

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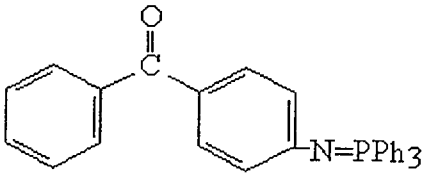

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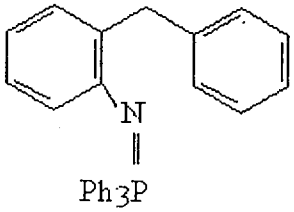

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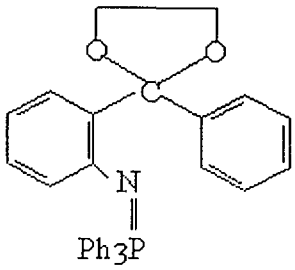

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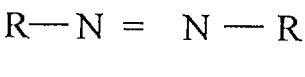

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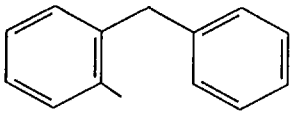
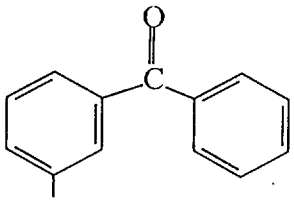
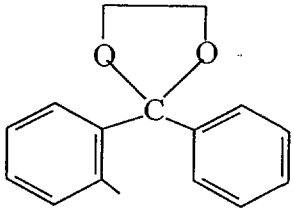
R = 

= 

= 

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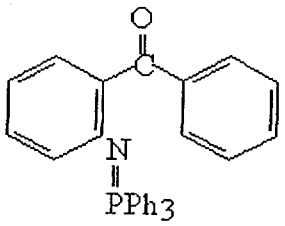

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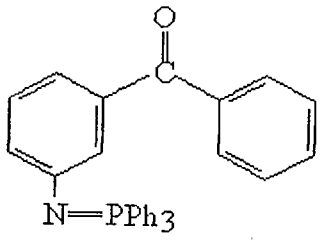

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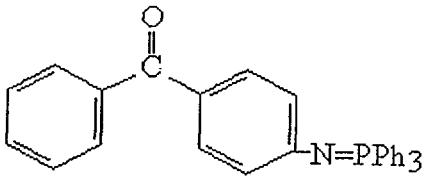

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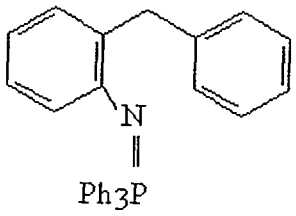

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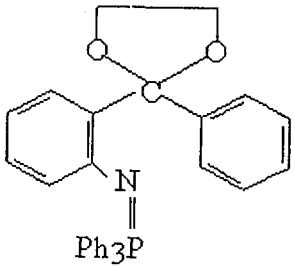

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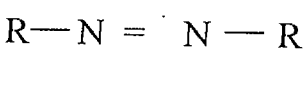

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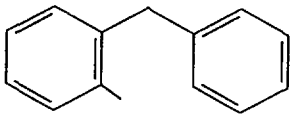
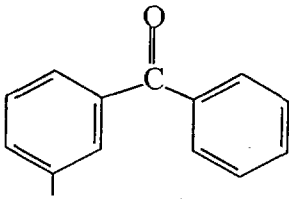
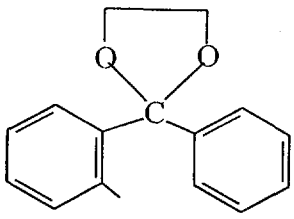
R = 

= 

= 

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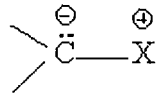
CHAPTER ONE

1. Introduction

Ylids are important class of compounds in which an atom from group V or VI of the periodic table bearing a positive charge, is connected to a carbon atom carrying an unshared pair of electrons-represented by the general formula :



The term "ylid" was first coined in the German language by Wittig in 1944. It was derived by use of the ending -yl to imply an open valence (i.e., a methyl) and the ending -id to emply anionicity (i.e., cetylid) both on a carbon atom.

The special characteristic of ylids that make them worthly of study in their own right is the unique stabilization afforded the carbanions by the presence of the adjacent 'onium 'atom group.

Thus, many ylids have been isolated as crystalline, stable substances where as normal carbonion are seldom isolable and are very reactive toward atmospheric components.

Ylids undergo two basic types of reactions, those in which only the carbanion is involved mechanistically and those in which both carbanion and the heteroatom portion are involved. The former group consists basically of those reactions which any carbanion, regardless of structure would undergo.

The presence of the heteroatom portion of the ylid usually is reflected only in its effect to the nucleophilicity exhibited by the carbanion. The usefulness of ylids in this type of reaction, is due mainly to their availability in a wide variety of structural environments. Since carbanion reactions inevitably are these which permit the formation of a new carbon-carbons bonds. The availability of almost any carbanion without worry of isomeric possibilities has been a boon to synthetic organic chemisty.

The most interesting reactions of ylids are the second group which involve both the carbanion and the heteroatom portion. The Wittig reaction

falls into this category and the discovery of this and related reactions incited the burst of activity in the field of ylid chemistry during the last decades studies of the mechanism of these reactions and of the physical properties of ylid have evoked interest in, and provided a substrate for the study of valence shell expansion by elements of the second and lower periods.

There are three main types, phosphorous, nitrogen and sulphur ylids although aresnic, selenium, etc ylids are also known. Because of P_{π}-d_{π} bonding, two canonical forms can be written for phosphorous and sulphur ylids, but for nitrogen ylids there is only one.

Once again, because of the resonance, phosphorous ylids are much more stable than the nitrogen ylids. Inspite of their resonance, sulphur ylids also have a low stability

$$R_3P = CR_2 \longleftrightarrow R_3P^{\oplus} - C^{\ominus} - R_2, \qquad R_2S = CR_2 \longleftrightarrow R_2S^{\oplus} - C^{\ominus} - R_2$$

Phosophorus ylids Sulphur ylids

$$R_3N^{\oplus} - C^{\ominus} - R_2$$

Nitrogen ylid

In almost all compounds which have P_{π}-d_{π} bonds, the central atom is connected to four atoms or to three atoms and an unshared pair of electron, to give tetrahedral structure. The P_{π}-d_{π} bond, therefore; does not change the geometry of the molecule, in contrast to the normal π bond which changes an atom from tetrahedral to trigonal.

1.1 The Wittig Reaction

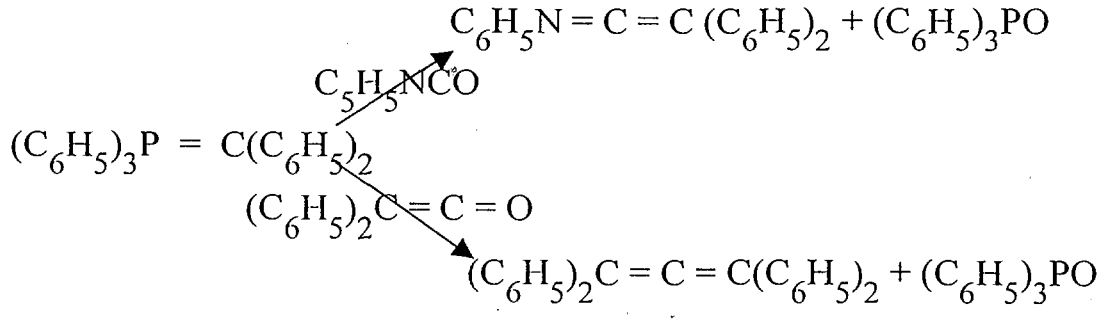
The Wittig reaction is named after professor George Wittig of the University of Heidelberge. The reaction involving a condensation of alkylidenephosphorane (R - alkyl, aryl) and carbonyl compound, followed by eliminatin of phosphine oxide from the intermediate betaine to give the olefin[1] (1).

$$R_3P = CR^1R^2 + R^3R^4CO \longrightarrow R_3P^{\oplus} - CR^1R^2 . C(O^-) R^3R^4$$
$$\longrightarrow R_3PO + R^1R^2C = CR^3R^4$$

(1)

The history of the development of the Wittig reaction was mentioned briefly by Wittig in his second review article in 1956[2], but has been discussed in more detail by him in a paper presented before the IUPAC symposium in organophosphorous compounds in May 1964[3].

The first condensation between a carbonyl compound and a phosphonium ylid was reported in 1919 by Staudinger and Meyer[4]. Who found that benzhydrylidenetriphenylphosphorane would react with phenylisocyanate to eliminate triphenyl phosphine oxide and form triphenylketenimine. Three years later, Luscher[5] found that heating the same ylid with diphenylketene afforded tetraphenylallene and triphenylphosphine oxide.



This reaction then lay dormant in the literature for twenty-seven years even though there were sporadic isolated investigation into the chemistry of phosphonium ylids in the interim.

In 1949 Wittig and Rieber[6] treated tetramethyl-phosphonium iodide with methyl lithium in hopes of obtaining pentamethylphosphorane, $(CH_3)_5P$. Instead, methylenetrimethylphosphorane, $(CH_3)_3 P = CH_2$(2), was formed and reaction with benzophenone afforded a betaine which was trapped as (2-hydroxy-2,2, diphenyl) ethyl trimethylphosphonium iodide(3) after quenching the reaction with acid and potassium iodide. Four years later, Wittig and Geissler[7] found that methyltriphenylphosphonium iodide like-wise could be converted to methylenetriphenylphosphorane, $(C_6H_5)_3P = CH_2$(4), with phenyl lithium, and that it would react with benzophenone to afford triphenylphosphine oxide and diphenylethylene(5) in 84% yield. This observation signaled the birth of the Wittig reaction..

$$(CH_3)_3P = CH_2 + (C_6H_5)_2CO \xrightarrow[(ii)\ H,KI]{(i)\ Ether} (CH_3)_3P^{\oplus}-\underset{OH}{\underset{|}{CH_2}}\ C(C_6H_5)_2I$$

(2) (3)

$$(C_6H_5)_3P = CH_2 + (C_6H_5)_2CO \xrightarrow{Ether} (C_5H_6)_2\ C = CH_2 + (C_6H_5)_3PO$$

(4) (5)

1.1.1 Phosphorous Ylids :

Phosphorous ylids have a general structure written as a resonance hybrid

The minimum structural requirement for a phosphorous ylid is that it contains an anionic carbon attached to a phosphorous atom which carries a high degree of positive charge. There is a variety of phosphorous structure which meets this minimum requirement but the most common is the phosphonium ylid, $R_3p = C$. As would be expected on the basis of the above, general formula phosphorous ylids these substances are reactive and, unless special structural features have been incorporated, are usually not capable of isolation. However, the number of isolable phosphorous yilds has risen sharply in recent years and permitted a detailed study of the yilds as pure substances.

Phosphorous ylids have a history reacting back to 1890's but virtually nothing was known of their chemistry until the 1950's with the exception of the results of a briefly study in 1920's. Michaelis and Gimborn[8] appear to have prepared the first phosphonium ylid, $(C_6H_5)_3\ P = CHCOOC_2H_5$, in 1894 although they proposed a different structure for the substance. They obtained the ylid by treatng an aqueous solution of triphenyl(carbethoxymethyl) phosphonium chloride with cold potassium hydroxide solution. Aksnes[9] subsequently has confirmed the ylid structure of the product. Staudinger[4] was the first to examine the reaction of ylids and his poineering experiments laid the ground work for the important synthetic application of phosphonium ylids developed much later by Wittig and his students.

1.1.2 Preparation of Akylidenephosphoranes :

(a) From Phosphonium Salts :

Alkylidenephosphorane (7) are obtained from alkylphosphonium salt (6) by the action of a suitable base.

$$R_3P^{\oplus} - CH_2\,RR'\ X^{\ominus} \xrightarrow{\text{base}} R_3P = CHR'$$

(6) (7)

The strength of base necessarily depends on the acidity of α-hydrogen and varies from aqueous sodium carbonate for the diphosphonium salt[10] $(ph_3P\text{-})_2\ CH_2Br^-$ to alkyl metals in non-polar solvents for unsubstituted alkyl-phosphonium salts. Bases and solvents commonly employed include butyl and phenyl lithium in ether, benzene or tetrahydrafuran and sodium or lithium alkoxide in the corresponding alcohol or in dimethylformamide. The use of dimethyl sulphoxide metallated by sodium hydride i.e., Meso-CH_2Na^+, with dimethyl sulphoxide as a solvent has been described. High yields of olefins are claimed from rapid reaction

Substituents on the α-and β-carbon atoms of alkyltriphenyl phosphonium salts can lead to complication in phosphorane formation.

(b) Other Methods :

Alkylidenephosphorane have also been obtained by the addition of carbenes to triphenylphosphine e.g.,

$$CH_2Cl_2 \xrightarrow{BuLi} [CH\,Cl] \xrightarrow{@\ Ph_3P} Ph_3P = CHCl$$

and by the thermal decomposition of the adduct of tripherylphosphuinc and diazo compound[4](8)

$$Ph_3P + Ph_2CN_2 \longrightarrow Ph_3P = N - N = NCPh_2 \xrightarrow{\Delta} Ph_3P = CPh_3 + N_2$$

Triphenylphosphine reacts with carbon tetrahalides at room temperature to give dihalogenomethylene (10) and dihalogenophosphorane[12,13](11). This involves the nucleophilic removal of halogen from the initially formed trihalogenomethyl phosphonium salt e.g.,

$$\underset{(9)}{Ph_3P + CBr_4} \xrightarrow{Cu_2Cl_2} [\,Ph_3P\ CBr_3\bar{B}r] \xrightarrow{Ph_3P} \underset{(10)}{Ph_3P = CBr_2} + \underset{(11)}{Ph_3PBr_2}$$

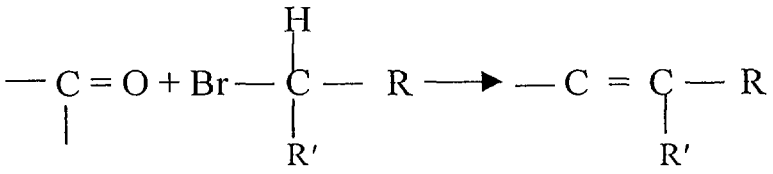
Stable phosphoranes of formula $Ph_3P{=}CXY$(X,Y= CN, CO_2R, COR) (13), can be obtained by the action of dichlorotriphenylphosphorane and triethylamine on compound containing a reactive methylene group[14] (12) e.g.,

$$\underset{(12)}{MeCO.CH_2.CO_2Et} + Ph_3PCl_2 \xrightarrow{2\,Et_3N} \underset{30\%\ (13)}{Ph_3P = C\,(CO_2\,Et)\,COMe}$$

1.1.3 The Characteristic Feature of Wittig Reaction :

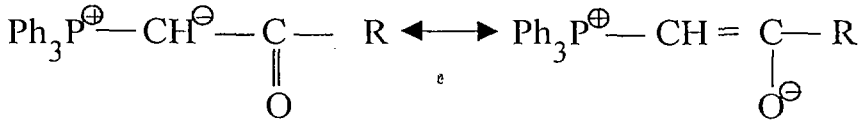
The important feature of the Wittig reaction is that, the reaction proceeds under mild conditions and the position of the resulting double bond is always certain. The synthesis has been applied without standing success in many fields, e.g., carotenoids, polyenes, vitamins D[15]. Recently, more attention has been paid to the mechanistic aspects of the synthesis, to the development of analogous olefin synthesis, and to the reaction of alkylidenephosphorane with functional groups other than carbonyl.

In the overall Wittig reaction, an olefin is formed from the aldehyde or ketone and an alkylhalide in which the halogen-bearing carbon contains at least one hydrogen.

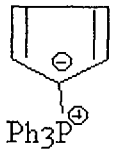


The reaction is very general, the aldehyde or ketone may be aliphatic, a licyclic, or a romatic (including diaryl-ketones); it may contain double or triple bonds; it may contain various functional group such as OH, OR, NR_2, aromatic nitro or halo, acetal, or even ester group[16]. Double or triple bonds conjugated with the carbonyl also do not interfere, the attack being at the C = O carbon. The phosphorous ylids may also contain double or triple bonds and certain functional groups. Simple ylids (R, R^1 = hydrogen or alkyl) are highly reactive, reacting with oxygen, water, hydrohalic acids, alcohol, as well as carbonyl compounds and carboxylic esters, so the reaction must be run under condition where these are absent.

When an electron-withdrawing groups, eg COR, CN, COOR, CHO, are present in the α position, the ylids are much more stable, because the charge on the carbon is spread by resonance.



These ylids react readily with aldehydes, but slowly or not at all with ketones. In extreme, case e.g. (14)



(14)

The ylid does not react with ketones or aldehydes. Besides these groups, the ylid may contain one or two α halogens[11] or an αOR or OAR group. In the latter case the product is an enol ether, which can be hydrolyzed to an

aldehycle[17] so that this reaction is a means of achieving the conversion of (15) to (16)

$$RCOR' \longrightarrow RR'CHCHO$$

(15) (16)

$$R''\ O\,CH_2Cl \xrightarrow{Ph_3P} R''\ OCH_2P^+Ph_3 \xrightarrow[RCOR]{base} R''\ OCH=\underset{\displaystyle R}{\underset{|}{C}}-R \xrightarrow{hydrolysis} R'-\underset{\displaystyle R}{\underset{|}{CH}}-CHO$$

However, the ylid may not contain an α nitro group. If the phosphonium salt contains a potential leaving group, such as Br or OMe, in the β position, treatment with a base gives elimination, instead of the ylid(17)

$$Ph_3P^+\,CH_2CH_2Br \xrightarrow{base} Ph_3\,P^+CH=CH_2 \qquad (17)$$

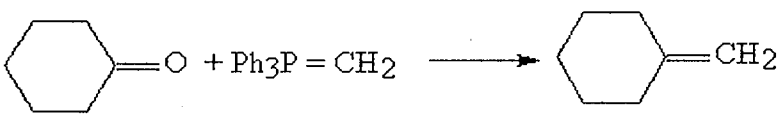
However, a βCOO- group may be present, and the product is a β, γ-unsaturated acid(18)

$$Ph_3P^+-C^-HCH_2COO^- + -\underset{|}{C}=O \longrightarrow -\underset{|}{C}=CHCH_2COO^-$$

(18)

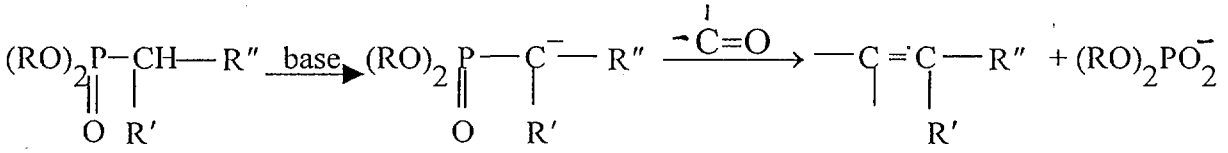
This is the only convenient way to make these compounds, since elimination by any other route gives the thermodynamically more stable α, β-unsaturated isomers. This is an illustration of the utility of the Wittig method for the specific location of a double bond. Another illustration is the conversion of cyclohexanone (19) to olefins cont aining double bonds[1](20)

e.g.



(19) (20)

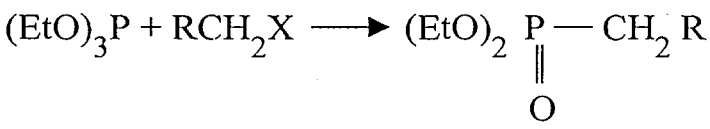
The Wittig reaction has been carried out with polymer supported ylids[19]. Ylids are usually prepared from triphenylphosphine, but other triaryl phosphine[20], trialkylphosphines[21] and triphenylarsine[22] have also been used. The Wittig reaction has also been carried out with other types of ylids, the most important being prepared from phosphonates[23](21)



(21)

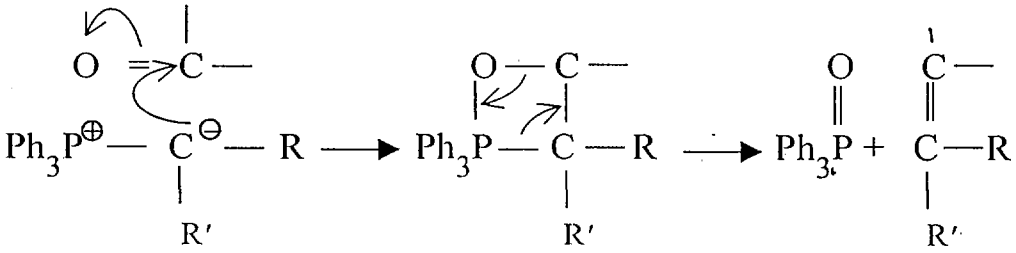
This method, sometimes called the Horner-Emmons, Wad sworth, or Wittig-Horner reaction[24] has several advantages over the use of phosphorane[25].

These ylids are more reactive than the corresponding phosphoranes, and when R' is an electron-withdrowing group, these copomunds often react with ketones that are inert to phosphorane. In addition, the phosphorous product is a phosphate ester and hence soluble in water, unlike phosphorous triphenyl oxide, which makes it easy to separate it from the olefin product phosphonates are also cheaper than phosphonium salts and can easily be prepared by the reaction[26] :



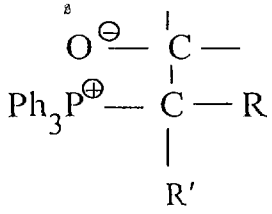
1.1.4 The Mechanism of Wittig Reaction :-

The mechanism of the key step of the wittig reaction is as follows[27] :



oxaphosphetane

For many years it was assumed that diionic compound called a betaine, is an intermediate on the pathway from the starting compound to the oxaphosphetane, no evidence for it[38], though many attepts have been made to find it.

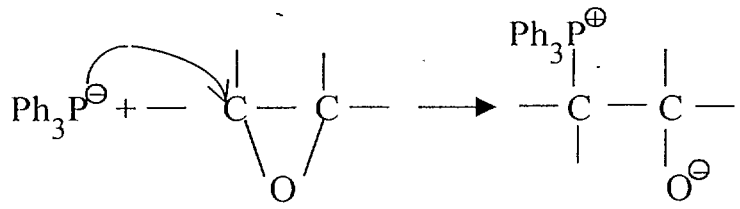


Betaine

"Betaine" precipitates have been isolated in certain Wittig reaction[29], but these are betaine-lithium halide adducts, and might just as well have been formed from the oxaphosphetane as from true betaine.

In contrast, there is much evidence for the presence of the oxaphosphetane, intermediates, at least with unstable ylids. For example ^{31}Pnmr spectra taken of the reaction mixture at low temperature[30] are compatible with an oxaphosphetane structure that persists for some time but not with a tetracoordinated phosphones species. Since a betaine, an ylid, and a phosphine oxide all have tetra coordinated phosphorous, these species could not be causing the spectra, leading to the conclusion that an oxaphosphetane intermediate is present in the solution. In certain cases oxaphosphetane have been isolated[31]. It has even been possible to defect cis and trans isomers of the intermediate oxaphosphetane by nmr spectrascopy[32]. According to this mechanism an optically active phosphonium salt R. R'R"P^{+} C+1 R_2 should retain its configuration all the way through the reaction, and it should be preserved in the phosphine oxide RR'R"PO. This has been shown to be the case[33].

The proposed betaine intermediates can be formed, in a completely different manner, by the nucleophilic substitution by a phosphine on an epoxide.

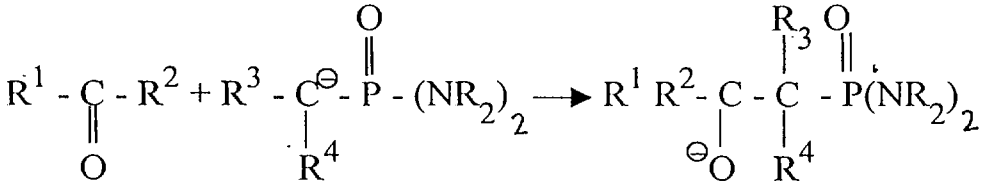


Betaines fromed in this way can be then converted to the olefin, and this is one reason why betaine intermediate were long accepted in the Wittig reaction.

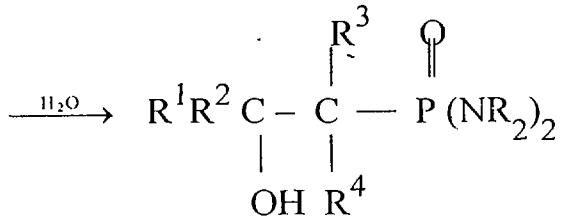
1.1.5 The Stereochemistry of Resulting Olefin :

Some Wittig reaction gives the z-olefin, some the E, and other give mixture, and the question of which factors determine the stereoselectivity has been much studied[34]. It is generally found that ylid containing stabilizing groups or formed from trialkylphosphines give E-olefins. However, ylids formed from triarylphosphine and containing stabilizing groups often give z or a mixture of z and E Olefins[35]. One explanation of this [38] is that the reaction of the ylid with the carbonyl compound is a 2+2 cycloaddition, which in order to be concerted must adopt the $[2_{\pi}s + 2_{\pi}a]$ pathway. This pathway leads to the formation of the more sterically crowded product, in this case the z Olefin.

If this explanation is correct, it is not easy to explain the predominant formation of E products from stable ylids but E compound are of course generally thermodynamically more stable than the z-isomers, and the stereochemistry seems to depend on many factors. The E : z ratio of the product can often be changed by a change in solvent or by the addition of salt[36]. Another way of controlling the stereochemistry of the product is by use of phosphonic bisamide. In this case the betaine (22) does form



(22)

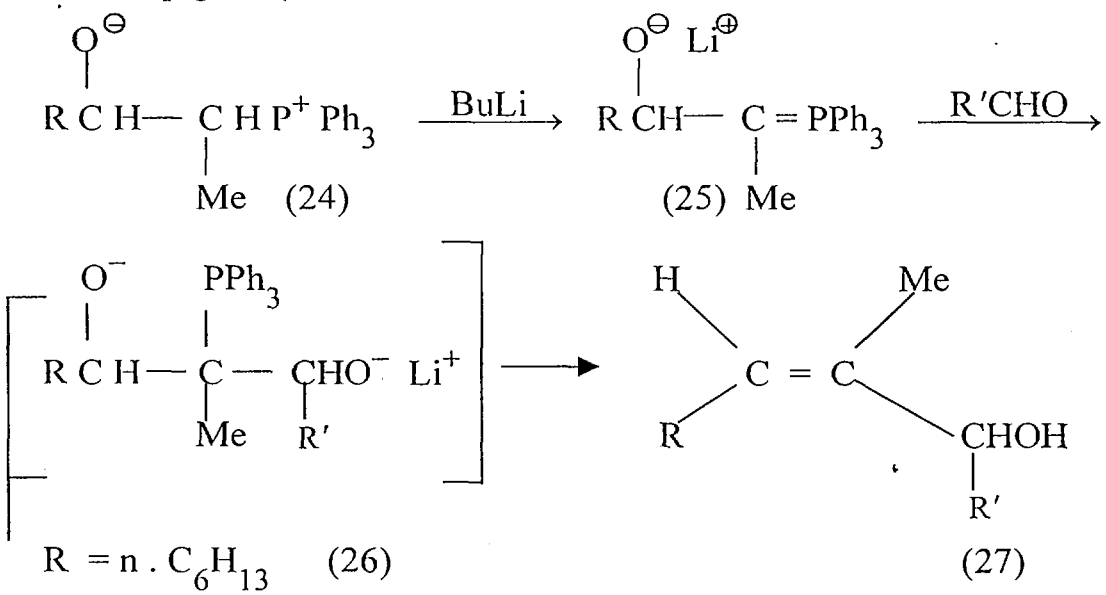


(23)

and when treated with water gives the β-hydroxyphosphonic acid bisamide (23), which can be crystallized and then cleaved to $R^1R^2C = R^3R^4$ by refluxing in benzene or toluene in the precence of silica gel[26].

compound (23) is generally formed as mixtures of diastereoisomers, and these mixture can be separated by recrystallization. Cleavage of the two diastereoisomers gives the two isomeric olefins. Optically active phosphonic acid bisamide have been used to give optically active olefin[37]. Another method of controlling the stereochemistry of the olefins (to obtain either the z or E isomer) starting with a phosphine oxide Ph_2POCH_2R has been reported[38].

In reaction where the betaine-lithium halide intermediate is present, it is possible to extend the chain further if a hydrogen is present α to the phosphorous. For example, reaction of ethylidene triphenyl phosphorane with heptanal at -78°C gave (24), which with butyl lithium gave the ylid (25). Treatment of this with an aldehyde R'CHO gave the intermediate (26), which after workup gave (27)[39].



(24) (25) (26) (27)

This reaction gives the unsaturated alcohol (27) stereoselectivity. (25) also reacts with other electrophiles, for example, treatment of (25) with N-chlorosuccinimide (NCS) or $PhICl_2$ gives the vinylic chloride RCH = CMeCl stereoselectivity. NCS giving the cis and $PhICl_2$ the trans isomer[40]. The use of Br_2 and $FClO_3$ (explosive reagent) gives the corresponding bromides and fluoride respectively[41].

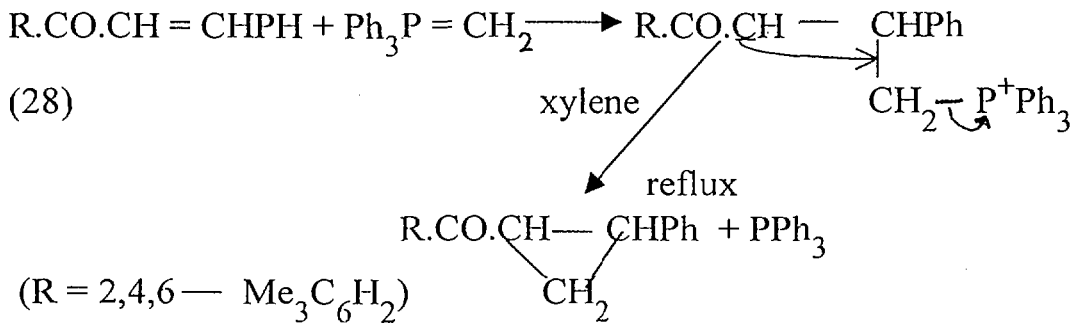
Reaction of (25) with electrophile have been called scopy reaction (α substitution plus carbonyl olefination via β - oxidophosphorous ylids)[42].

1.1.6 The Reactions of Alkylidenephosphoranes with Various Functional Groups :

Alkylidenephosphoranes are powerful nucleophlic agents and react with a range of functional groups, comparable to those reacting with Grignard reagent.

(a) Aldehydes and Ketones :

In contrast with Grignard reagents and with some sulphur ylids, alkylidene-phosphoranes normally attack at the β-position of α, β unsaturated ketones, only when the carbonyl group is highly hindered in the ketone (28)[43].



(28)

(R = 2,4,6— $Me_3C_6H_2$)

Subsquent elimination of triphenylphosphine then gives cycloproyl ketone.

(b) Inorganic Reagents :

Strongly basic alkylidenephosphoranes react rapidly with water to give phosphonim hydroxides which then decompose to phosphine oxide and hydrocarbon, the latter being formed from that radical which most stable as the anion, e.g.,

$$Ph_3P = CH_2 \xrightarrow{H_2O} Ph_3P^{\oplus} MeOH^- \longrightarrow Ph_2MePO + PhH$$

$$Ph_3P = CHPh \xrightarrow{H_2O} Ph_3P^{\oplus} - CH_2PhOH^- \longrightarrow Ph_3PO + PhMe$$

with mineral acid the corresponding phosphonium salt is obtained Halogens give the α-halogenoalkylphonium salts[44]. e.g.,

$$Ph_3P = CHPh \xrightarrow{O_2} Ph_3PO + [PhCHO] \qquad Ph_3P = CHPh \longrightarrow PhCH=CHPh(55\%)$$

(29) (29) Alkylidenephosphoranes form adducts with boron compounds (alkyls, halides, and hydrides)[45] and react with metal and non-metal halides to give the expected phosphonium salts [(29) ; M = Si, Ge, Sn, Hg, Zn, P and Sb]

$$Ph_3P = CH_2 + -\underset{|}{M}-X \longrightarrow Ph_3P^{\oplus} - CH_2 - M - X \quad (29)$$

(c) Alkyl Halides :

(29) These react with alkylidenephosphorane to give c-alkylated phosphonium halides, e.g., isopropylidene triphenylphosphorane with methyl iodide gives kriphenyl-t-butyl phosphonium iodide. Intramolecular alkylation is successful[46] e.g.,

$$Ph_3P^{\oplus} - [CH_2]_5 - CH_2\,BrBr^- \rightarrow Ph_3P = C_6H_{10} \xrightarrow{[O]} C_6H_{10}O$$

[14%]

(d) Esters, Acid Halides, etc :

Esters, thioesters[47], acid halides[48], and N-ethylamidazoles[49,50], react with alkylidenephosphoranes to give initially the β-ketoalkylphosphonium salts (30). When X = OR or SR, these elminate XH; when X = halogen or imidazole, ylid exchange occurs with a second molecule of phosphorane. In any case the product is the stable β-Ketoalkylidenephosphorane(31)

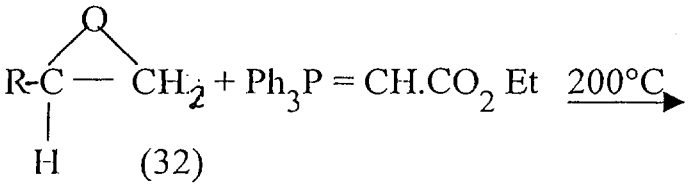
$$Ph_3P{=}CHR + RCOX \longrightarrow Ph_3P^{+}{-}CHR{-}CORX^{-} \xrightarrow{-HX} Ph_3P{=}CR{-}COR$$

(30) (31)

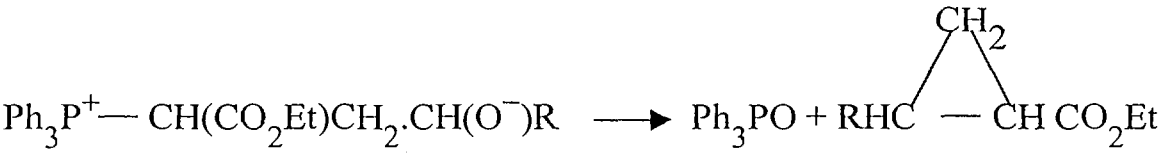
The corresponding ketones, RCH_2COR', can be obtained from these either by hydrolysis, by reduction with zinc and acetic acid, or by electrolytic reduction and a mercury cathode.

(e) Epoxides :

Denney and Boskin[51] treated the epoxide [(32) R = Ph , C_6H_{13}] with the phosphorane ester (33) under vigorous conditions and obtained cyclopropanes in moderate yields



(32)



(f) Carbon - carbon Double and Triple Bonds : -

Alkylidenephosphoranes add to activated carbon-carbon double bonds as in [(34) R^4 having - M effect] to give intermediate (35) which may then react in one of three ways depending on the nature of the substitutents

$$Ph_3P{=}CHR^1 + R^2R^3C{=}CR^4{}_2 \longrightarrow Ph_3P^{+}{-}CHR^1.CR^2R^3.\bar{C}{-}R^4{}_2$$

(34) (35)

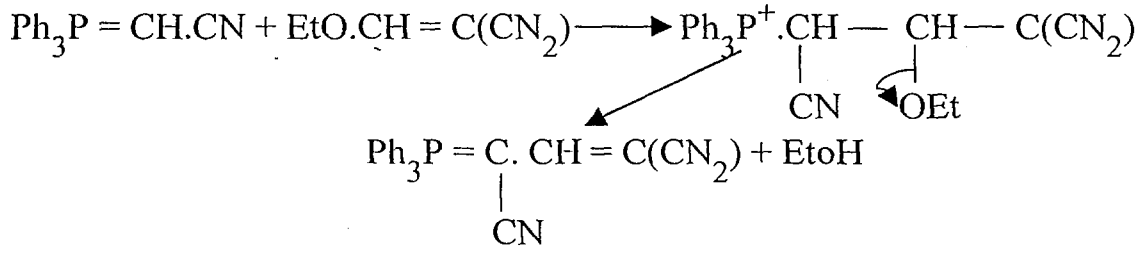
when R^1 has a -M -effect, transfer of a proton from the α to β-carbon leads to a new stable phosphorane[52] e.g.

$$Ph_3P{=}CH.CO_2Me + PhCO.CH{=}CH.CO_2Me \longrightarrow$$

$$Ph_3P{=}C(CO_2Me)\,CH(CO_2Me)\,CH_2COPh$$

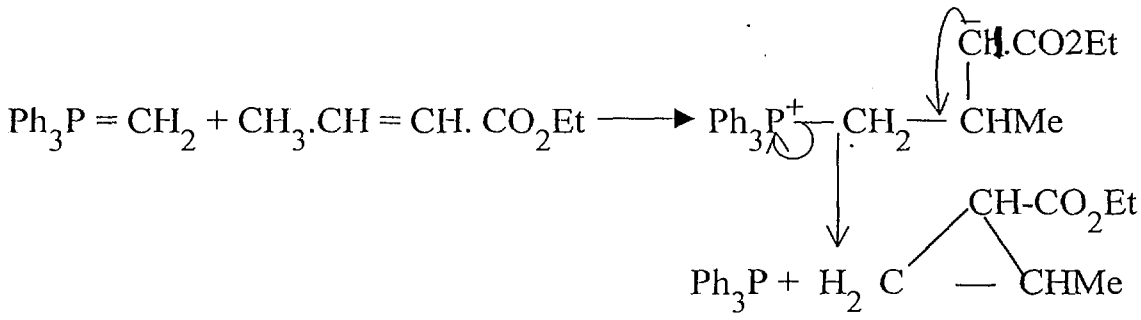
92%

when R^2 is capable of forming a stable anion, the intermediate eliminates R^2 – which then abstracts the α-proton to give a new stable phsophorane[53]. e.g.,



(78%)

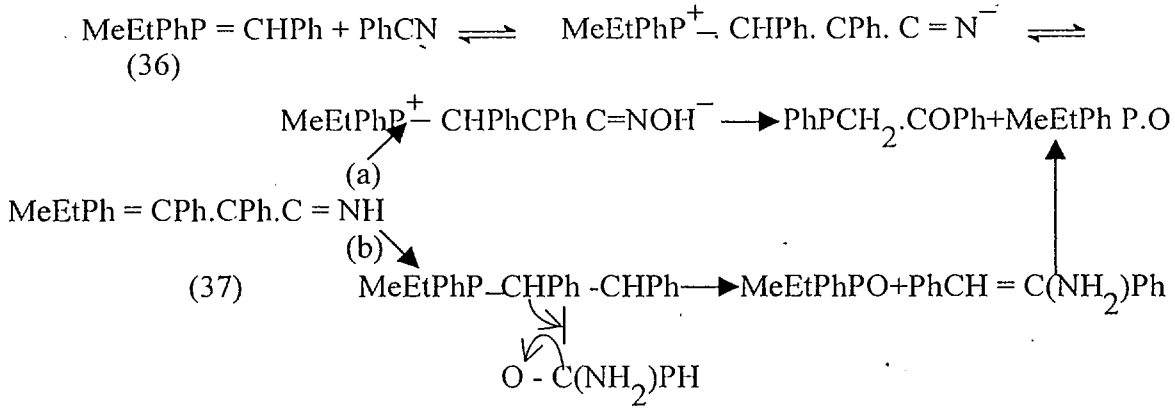
Finally, if neither of the above feature is present, the intermediate may eliminate triphenylphosphine to form a cyclopropane[52,54] e.g.,



(91%)

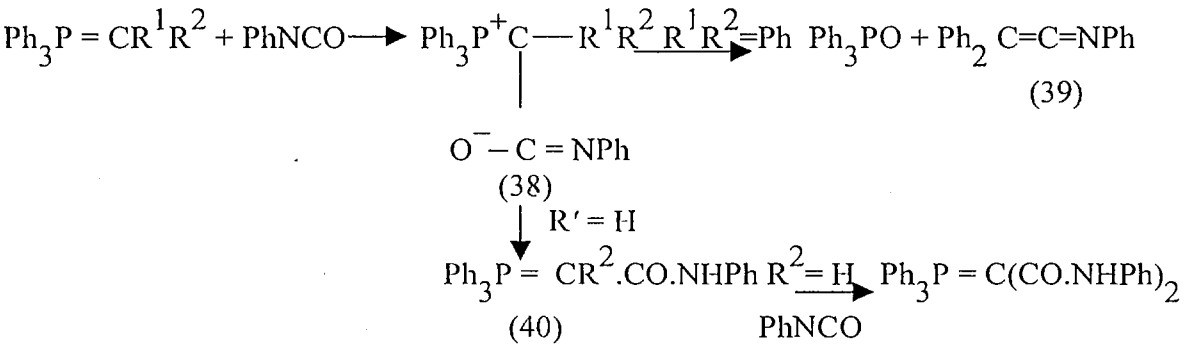
(g) Cyanides :

When the optically active benzylidene-phosphorane (36) is treated in ether with benzonitrile[56] the characteristic orange colour of the reagent is not discharged, but hydrolysis of the reaction mixture with methanolie potassium hydroxide gives deoxybenzoin (78%) and phosphine oxide (71%) with activity indicating that inversion of configuration has occured to the extent of 68%. Two competing reactions are envisaged for the hydrolysis of the betaine (37), (a) involving inversion and (b) involving retention of configuration around the phosphorous atom.



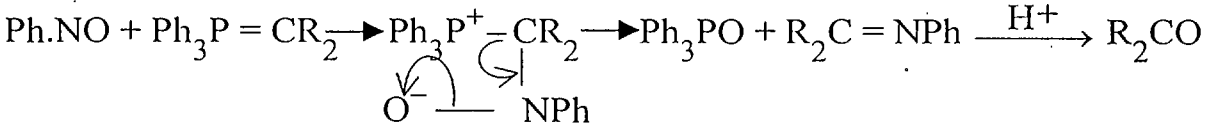
(h) Isocyanates: -

Alkylidenephosphoranes add to phenyl-isocyanate[55]. to give the betaine (38). When R^1 and R^2 are both phenyl, a normal Wittig reaction then gives imidoethylene (39), but, if either R^1 or R^2 is hydrogen, migration of that hydrogen to nitrogen occurs to give more stable phosphorane (40). With the methylene phosphorane (when $R^1 = R^2 = H$) this process is then repeated with a second molecule of isocyanate



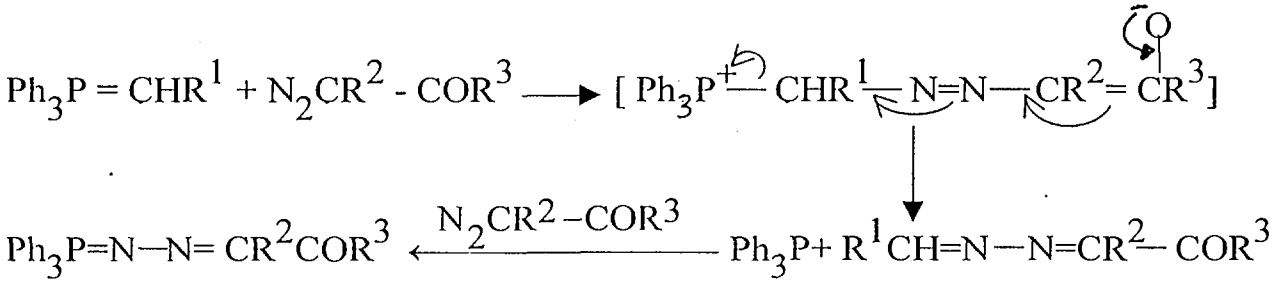
(i) Nitroso-Compounds :-

Alkylidenetriphenylphosphoranes react with nitroso benzene as in a normal olefin synthesis to give phosphine oxide and anils[57]. As these are readily hydrolysed to carbonyl compounds this gives a convenient method converting RRCHBr into RRCO, e.g., geranyl bromide into citral (74% from the phosphonium salt)

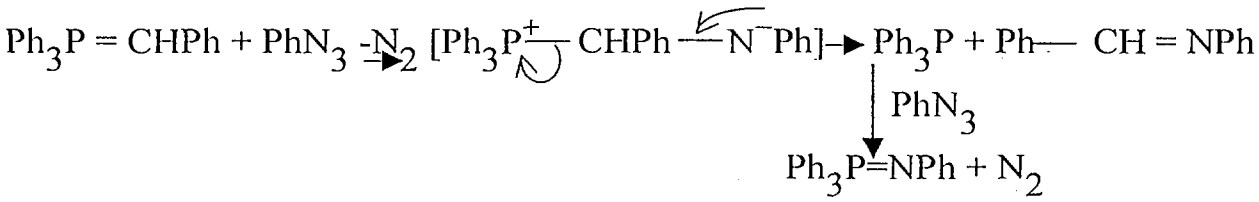


(j) Diazo-Compounds, Diazonium salt and Azides :

Compounds containing electrophilic nitrogen react with alkylidene phosphoranes in the expected way. Diazo-ketones and the more reactive phosphoranes give intermediates which eliminate triphenylphosphine, as shown, to form mixed azides[58]. The phosphine then reacts with a second molecule of diazoketone.

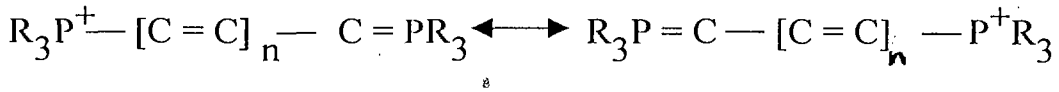


The intermediates from azides and alkylidenephosphorane eliminate triphenylphosphine to form schiff's bases[59]. The phosphine then reacts with a second molecule of azide if available :

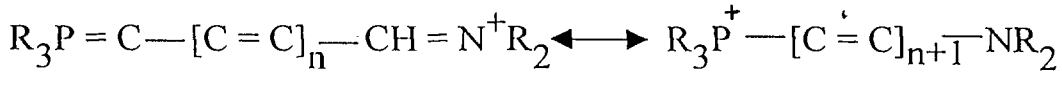


(k) The preparation of phosphorous ...Containing Dyes :-

The Gevaert group of workers[60] have prepared, from stable alkylidene phosphoranes, dyes containing the chromophores (41 - 43).



(41) "Phosphinines"



(42) "Phosphocyanines"

(43) "Merophosphinines"

1.2 Iminophosphoranes :

Historically, the iminophosphoranes, $R_3P : NR$, have presedent over the alkylidenephosphoranes, $R_3P : CR_2$, which they closely resemble in their reactions[60].

Iminophosphoranes can be represented as resonance hybrids of the two contributing structure (44a) and (44b), the nature of the multiple bonding between the nitrogen and phosphorous atoms depending on the degree of overlap of the filled nitrogen 2p-orbital(s), with vacant phosphorous 3d-orbitals)

$$R_3P^{+}—N^{-}R \longleftrightarrow R_3P = NR$$

a (44) b

Some quanitative information is available regarding the chemistry of iminophosphoranes but virtually nothing is known about the quantitative aspects of their chemistry.

I.2.1 The Structure of Iminophosphorane :-

There has been no systematic investigation of the variation in the properties and structure of the iminophosphoranes with a change in substituents. In addition, there have been relatively little physical data uncovered, the most interesting feature of the iminophosphorane of course is the nature of phosphorous-nitrogen bond. An x-ray analysis will be required to determine the geometry about this bond.

The hybirdization about the phosphorous most likely is very similar to that in phosphonium ylid tetrahedral hybridization with any multiple bonding occuring by overlap of the appropriate filled nitrogen orbitals with about 3d-orbitals of the phosphorous atom. The nitrogen atom of an iminophosphorane could be trigonally hybridizied, the P-N-R bond being near 120° with lone pair in an sp^2-hybrid orbital and the other in a p orbital (Fig. 1)

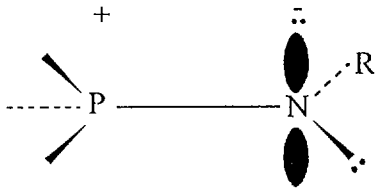


Fig. (1) Trigonal hybridization of phosphinimine

Tetrahedral hybridization of the nitrogen would result in a P-N-R angle of 109.5 with both unshared pairs in sp^3 hybrid orbital (Fig.2).

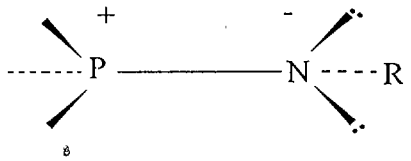
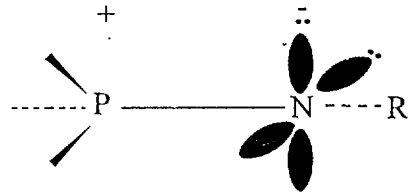


Fig. (2) Tetrahedral hybridization of phosphinimine

Digonal hybridization would result in a P-N-R angle of 180° with both lone pair being in p-orbital (Fig. 3)



The dipole moment of N-phenyliminotriphenyl phosphoran is 4.4d very close to that of triphernylphosphine oxide[62] (4.3d). The polarity of the phosphorous - nitrogen bond must be some what greater than the phosphorous - oxygen bond. Since it has as high a dipole moment inspite of the lower electronegativity of nitrogen than oxygen. The imines appear to be more basic and more nucleophilic than the phosphrine oxide in agreement with this supposition.

The phosphonus-nitrogen stretching frequency occurs in the infrared[163] region at 1160 - 1180 cm very close to that for the phosphorous-oxygen bond. There have been no correlation of structure with frequency as yet and insufficient data are available to begin here. The ultraviolet spectrum of N-phenyliminotriphenyl phosphorane had little character to it but much less than triphenyl phosphine or its oxide. It does have a yellow colour with absorption tailing off in the 350 mμ region. The N-(p-substituted phenyl) iminotriphenyl

phosphoranes do exhibit maxima in the ultra-voilent region extended from about 260mm for the p-chloroimine to about 430mm for the p-nitroimine. These bands and the shifts they show reflect conjugation between the imine nitrogen and the phenyl substituent.

Practically no 31p NMR data has been recorded for imino phosphoranes. The unique bis-imine (45) and the bis-ylid (46) showed almost identical shfits[65]. Both showed single resonance lines, which indicated that both phosphorous atoms were similarly shielded . In sufficient spectra have been obtained in either ylids or imines to permit correlation

$(C_6H_5)_3P^+ - N^- - P^+(C_6H_5)_3\ Br^-$ $\quad$ $(C_6H_5)_3P^+ - \overset{|}{C}\text{-H-}P^+(C_6H_5)_3Br^-$

δ = -21 ppm $\quad$ δ = -21.2 ppm

(45) $\quad$ (46)

All of the N-substituted and unsubstituted triaryl used trialkylimino phosphoranes are monomeric in solution[66]. The only phosphinimines that have been shown to be dimeric are those which have trihalophosphorous groups.

Not even all of the N-substituted iminotrihalophosphorane are dimeric but only those which carry substituents on nitrogen which are not powerfully electron-withdrawing. Thus the N-phenyl and hte N-methylimino triphenylphosphoranes are the only ones which have been shown to be dimeric to date[67,68]. The N-(2,4-dinitrophenyl) and the N-(P-toluene sulphonyl) derivatives are monomeric[69, 70].

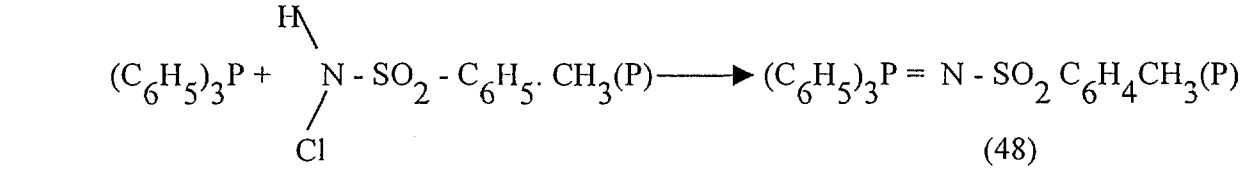
The iminophosphoranes have shown no indication of thermal instability with but one exception. Apple and schllhorn[71] have found that the bis-imine (47) decomposed upon warming to nitrogen and triphenyl phosphine. The deriving force must be the formation of molcular nitrogen[66].

$$(C_6H_5)_3P^+ - \ddot{N}^- - \ddot{N}^- - P^+(C_6H_5)_3 \longrightarrow 2\,(C_6H_5)_3P + N_2\uparrow$$

(47)

I.2.2 Preparation of Iminophosphoranes :

Three different methods have been used for the preparation of iminophosphoranes. One of the earliest methods was exemplified by the reaction between triphenylphosphine and chloramine-T in ethanolic solution to afford N-p-toluene sulphonyl Triphenyl Phosphorane (48),[72]. This reaction afforded crystalline imide in good yield from a variety of substituted triphenyl phosphines.

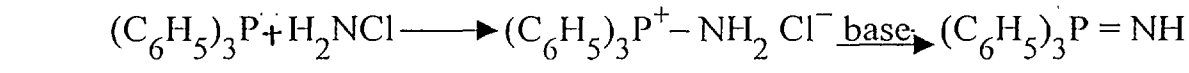


$$(C_6H_5)_3P + \begin{matrix} H \\ \diagdown \\ N - SO_2 - C_6H_5.\ CH_3(P) \\ / \\ Cl \end{matrix} \longrightarrow (C_6H_5)_3P = N - SO_2\ C_6H_4CH_3(P)$$

(48)

The reaction probably proceeded via nucleophilic attack of the phosphine on nitrogen to form an amido-phosphonium salt which was deprotonated.

Reaction of Chloramine and tripherylphosphine also afforded an amino phosphonium salt[66, 73, 74]. The latter group found that this salt could be deprotonated with sodamide to (49). Sisler, et al[75], effected the same conversion but in the presence of magnesium hydride.



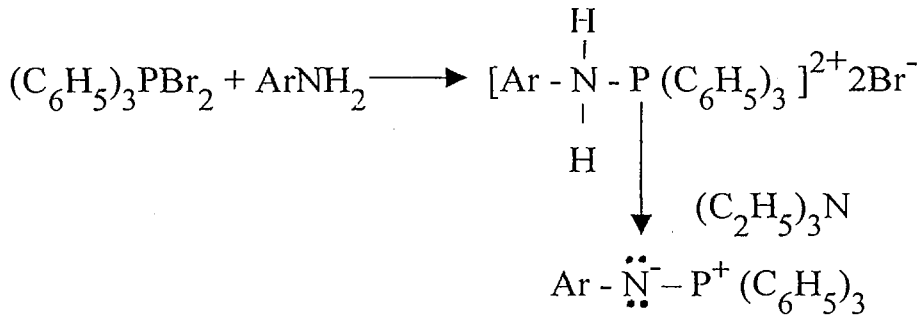
$$(C_6H_5)_3P + H_2NCl \longrightarrow (C_6H_5)_3P^+ - NH_2\ Cl^- \xrightarrow{\text{base}} (C_6H_5)_3P = NH$$

(49)

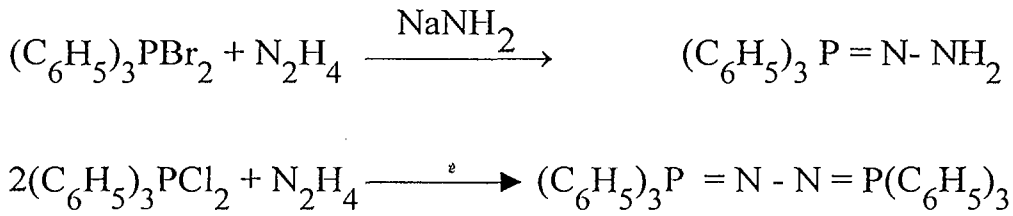
Iminophosphoranes could be prepared from a variety of tertiary phospheines by this method. All attempts to effect the deprotonation of the aminophosphonium salts in a queous media led to hydrolysis and the formation of tertiary phosphine oxide and ammonia.

Horner and Oediger[63] developed a second method for the preparation of iminophosphoranes one that is, in general, the most widely applicable of the three methods to be discussed. Reaction of a wide range of primary aryl amines with triphenylphosphine dibromide in the presence of two equivalents of triethylamine afforded the imines in 70% yield. The reaction probably

involved the attack of the amine on phosphorous followed by two deprotonation.



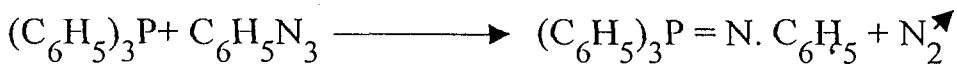
Zimmer and singh[76] have shown that this reaction also can be applied to the preparation of N-alkylimino triphenylphosphorane using sodamide as a base. Similarly reaction of the triphenyl phosphine dibromide with hydrazine in the presence of sodamide afforded N-aminoimino triphenyl phosphorane, but use of excess phosphine dihalide afforded the bis-imine (50)[76].



(50)

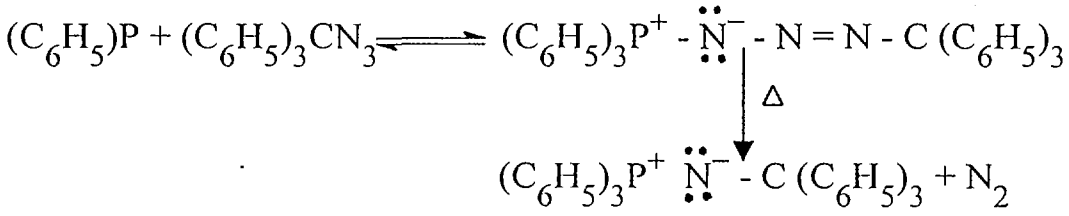
In all examples of the reaction of phosphine dihalides with amino compound there have not developed any limitation in the nature of the amino compound that can be employed.

The reaction of organic azides with tertiary phosphine is the oldest known method for the preparation of iminophosphoranes. Staudinger and Meyer[4] found that warming phenylazide with triphenylphosphine led to the evolution of nitrogen and the formation of crystalline N-phenyliminotriphenyl phosphorane.



They applied this reaction to several other organic azides, for example, prepared N-benzoyliminotriphenylphosphorane from benzoylazide it appears that the scope of the reaction between phosphines and oxides for the synthesis of iminophosphoranes is limited only by the availability of the requistic reactants.

The mechanism of the reaction between tertiary phosphine and azides probably involves nucleophilic attack by the phosphine on the azide nitrogen. There have been several successful attempts to isolate the initial adducts from the reaction. Bergmann and wolff[71] reported that triphenylmethylazide and triphenylphosphine reacted in ether solution to afford an adduct of m.p. : 104 - 105°, which retained all three nitrogen atoms. Heating of this adduct was reported to result in the loss of nitrogen and the formation of N-triphenylmethylimino-triphenylphosphorane (51). No characterization was reported for the amine but it was found to react with ketene to afford a schiff's base, a'reaction characteristic of other iminophosphoranes[71]

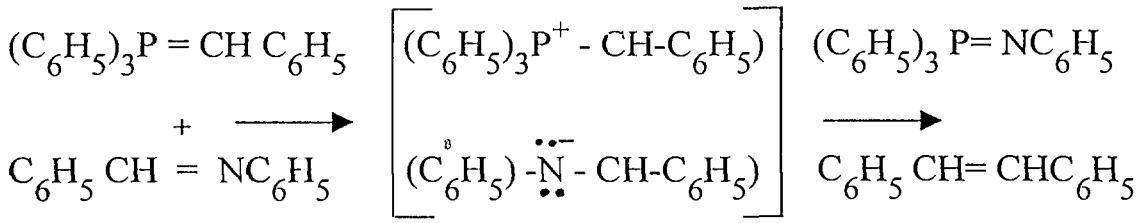


(51)

Staudinger and Hauser[78] reported that triphenyl phosphine and hydrazoic acid afforded aminotriphenyl phosphonium azide, but this result was questioned by Leffer[79] who in turn proposed phosphatetrazole structures. Cookson and Hughes[80] have confirmed the original assignment by detection of the azide ion. An oxidation-reduction must take place since nitrogen is evolved in the reaction.

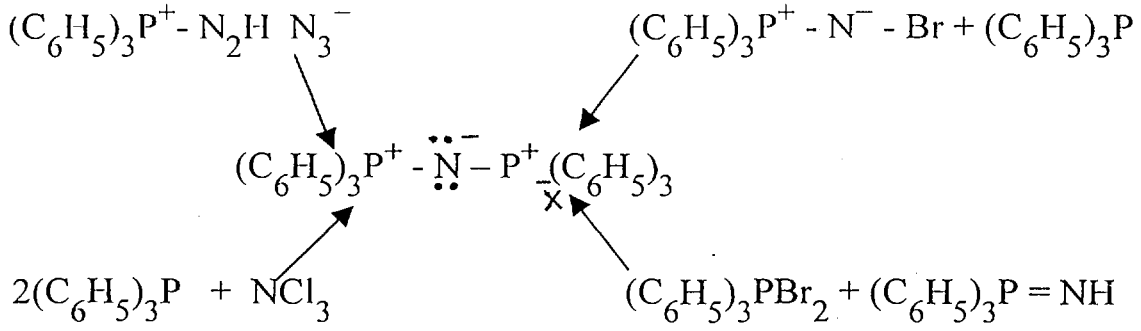
Bestmann and Seng[81] have reported an interesting reaction which resulted in the conversion of a methylene-phosphorane into an iminophosphorane. Benzylidene triphenyl-phosphorane and benzylidene

aniline afforded pheynylimino triphenyl phosphorane and stilbene, presumelly by way of a betaine similar to those encoutered in the Witting reaction.



There have been four reports of the preparation of the bisimine (52). Appel etal.[82] found that triphenylphosphine and bromoiminotriphenyl phosphorane afforded the bromide salt of (52). The same salt was obtained when triphenylphosphine dibromide was treated with iminotriphenyl phosphorane. Appel and Buchler[83]. obtained the chloride of (52) from two moles of triphenylphosphine and one mole of nitrogen trichloride. Cookson and Hughes[80] obtained the azide of (52) by heating aminotriphenyl phosphonium azide.

The bis-imine is isoelectronic with the hexaphenylcarbodiphosphorane obtained by Ramirez[84] , but the former is considerably more stable.



(52)

The three general methods for the synthesis of the iminophosphoranes, the phosphine displacement on a substituted amine the amine displacement on a phosphine dihalide and the reaction between an azide and a phosphine all have proved sufficiently versatile to date. The latter method probably is the most straight forward, but the second method perhaps is the most flexible.

1.2.3 Reaction of Iminophosphoranes :

There are two basic types of reactions known for the iminophosphorane, first, their reactions as ordinary nucleoplic in which the phosphorous atom plays no discrete role, and, second their reactions as nucleophlilies in which the phosphorous atoms plays a direct role usually involving its transitory pentavalency. In both of these cases the reactions of iminophosphorane parallel those of the methylene phosphoranes rather closed although much remains to be done in elucidating the detailed mechanism of most of the reactions.

The outstanding chemical property of the iminophosphorane is their nucleophilicity but the most interesting properties are those that depend on a combination of a nucleophilic reaction and an elimination of the phosphorous group in an oxidized state. In other words, those reactions which take advantage of the availability of the vacant 3d orbitals of phosphorous.

Iminophosphoranes are readily protonated to the corresponding aminophosphonium salts in the presence of mineral acids[78,85]. Numerous salts have been characterized[73].

There have been no quantitative studies on the relationship of basicity to molecular structure but they would be expected to parallel the behaviour of phosphonium ylids

$$(C_6H_5)_3P^+ - \bar{N} - R \underset{-H+}{\overset{H+}{\rightleftharpoons}} [(C_6H_5)_3 P- NHR]^+$$

A qualitative relationship is apparent from the observation that sodamide is required to form iminotriphenylphosphorane from its conjugate acid[74], while triethylamine will form N-phenyliminotriphenyl phosphorane from its conjugate acid[63]. Therefore, the N-phenylimine appears to be the least basic.

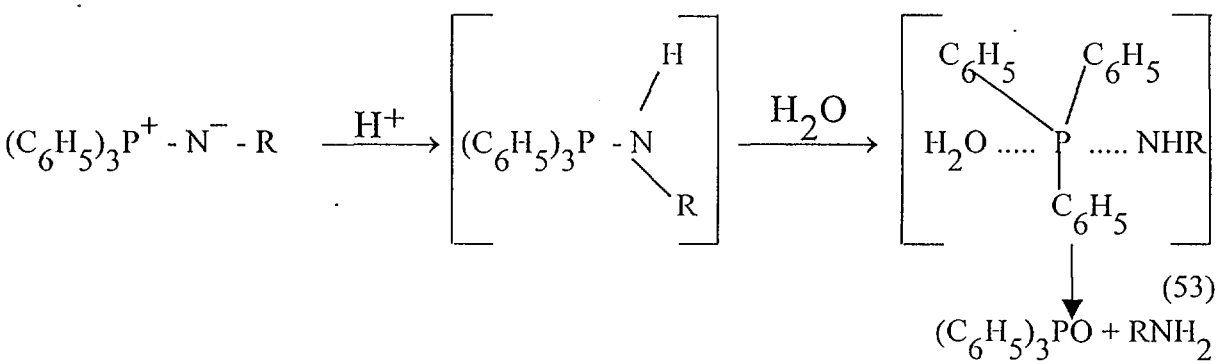
Its conjugate acid the most acidic, probably due to stablization afforded the imine by delocalization of unshared electrons through the phenylring.

Iminophosphorane are prone to hydrolyze. The case with which the hydroloysis occurs seem to be correlated to the basicity of the imine. Simply upon exposure to the atomsphere iminotriphenylphosphorane is hydrolysed to ammonia and triphenylphosphine oxide[66, 75]. On the other hand, N-aryliminotriphenyl-phosphoranes are stable on exposure to the atomsphere and in aqueous solution but are hydrolyzed rapidly in dilute acid media[4]

$$(C_6H_5)_3P = NH \xrightarrow{H_2O} (C_6H_5)_3PO + NH_3$$

$$(C_6H_5)_3P = NAr \xrightarrow[H^+]{H_2O} (C_6H_5)_3PO + ArNH_2$$

The mechanism of the hydrolysis of iminophosphoranes probably involves the initial protonation of the imine to form a salt followed by attack of water or hydroxide on phosphorous, via a pentavalent intermediate (53) to form the phosphine oxide and amine. Horner and winkler[86] have shown that the phosphorous atom in such hydrolysis mainly is inverted in agreement with this proposal when the imine was alkylated first and then hydrolysed under the conditions the oxide product was exclusively inverted.

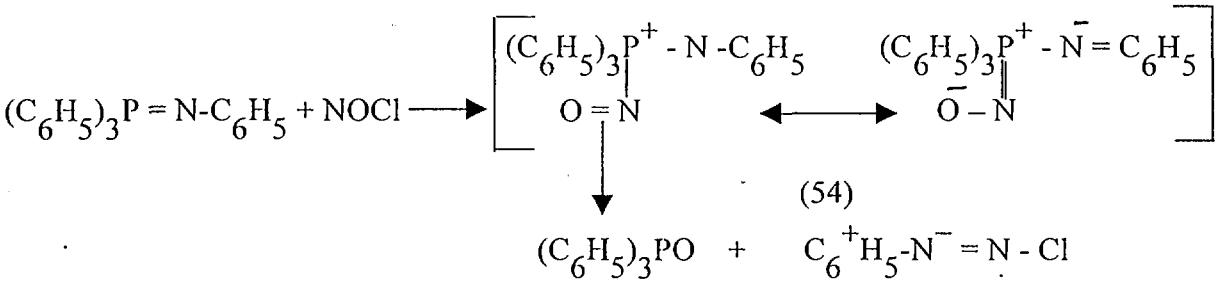


Phosphinimes will undergo reaction with a variety of Lewis acids. Crystalline and stable adducts were formed with a variety of boron cmpounds such as boron trifluoride[87, 88], triphenylboron[87], and diborane[89]. As a result

of their nucleophlicity imine also have served as figand in metal complexes such as $[(C_6H_5)_3P = NH]_2COCl_2$ and the cupper (ii) analog[90].

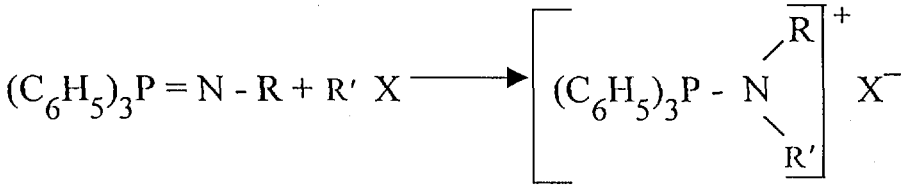
Zimmer and Singh[91]. reported an interesting reaction between N-phenyliminotriphenylphosphorane and nitrosyl chloride which afforded triphenyl phosphine oxide and phenyl diazonium chloride at -70c°. Zimmer had proposed the intermediacy of N-nitrosoamidophosphonium salt (54) which eliminated triphenylphosphine oxide via a four-membered transition state similar to that involved in the Wittig reaction.

This mechanism predicted the phosphorous atom to retain its configuration



(54)

Iminophosphoranes can be readily alkylated with alkylhalides. Reaction of equimolar amounts of imines and alkyl halide leads to formation of the corresponding N-alkyl aminophosphunium salt[71, 76, 85].



Halogination of iminophosphoranes proceeded in a some what analogous manner. Reaction of (55) with chlorine, bromine or iodine afforded one-half equivalent of the corresponding N-halo-iminotriphenyl phosphorane, all of which are crystalline compound that the reaction involved the initial nucleophilic attack of the imine on halogen was evident from the formation of the N-iodoimine from iodine monochloride and (55)

$$(C_6H_5)_3P = NH + X_2 \longrightarrow [(C_6H_5)_3P^+ - NHX\ X^-] \xrightarrow{(55)} (C_6H_5)_3P = N\text{-}X$$

(55)

$$2(C_6H_5)_3P = NH + I - Cl \longrightarrow (C_6H_5)_3P = NI + (C_6H_5)_3\ P^+ - NH_2Cl^-$$

Iminophosphoranes have been shown to react with carbonyl compounds to form schiff's bases and phosphine oxides in a manner reminiscent of the Wittig reaction. The first report of this reaction was by Staudinger and Meyer[4] in 1919 who found that N-phenyliminotriphenyl phosphorane (56) reacted with triphenyl ketene to afford triphenyl ketenimine (57), identical to that formed from benzhydrylidene triphenylphosphorane and phenyl isocyanate. The scope of this reaction was expanded to include reaction of (56) with benzophenone, benzaldehyde and phenylisocyanate, all of which involved in the replacement of a carbonyl oxygen by N-phenylimino group.

$$(C_6H_5)_3\ P = NC_6H_5 \quad + \quad (C_6H_5)_2C = C = O$$

(56) ↓

$$(C_6H_5)_2\ C = C = NC_6H_5 \quad + \quad (C_6H_5)_3PO$$

(57) ↑

$$(C_6H_5)_3P = C(C_6H_5)_2 \quad + \quad C_6H_5N = C = O$$

The same group[4, 61] found that (56) reacted with carbon dioxide and carbon disulphide to form an isocyanate and an isothiocyanate respectively. Reaction of N-phenyliminotriphenyl phosphorane with carbon dioxide, however, afforded N, N-diphenylcarbodimide presumably via the intermediacy of phenylisocyanate which reacted with additional imine[78]. An analogous conversion of N-glucosylimino triphenyl phosphorane to a carbodimide was reported by Messmer[92].

$$(C_6H_5)_3\ P = N.C_6H_5 + (C_6H_5)_2CO \longrightarrow (C_6H_5)_2\ C = N.C_6H_5 + (C_6H_5)_3PO$$

(56)

$$(56) + C_6H_5CHO \longrightarrow C_6H_5\text{-}CH{=}N.C_6H_5 + (C_6H_5)_3PO$$

$$(56) + C_6H_5NCO \longrightarrow C_6H_5.N = C = NC_6H_5 + (C_6H_5)_3PO$$

$$(56) + CO \longrightarrow C_6H_5.N = C = O + (C_6H_5)_3PO$$

$$(56) + CS_2 \longrightarrow C_{36}H_5.N = C = S + (C_6H_5)_3PO$$

$$2(C_6H_5)_3P = N.C_6H_5 + CO_2 \longrightarrow C_6H_5.N{=}C{=}N.C_6H_5 + 2(C_6H_5)_3PO$$

Appel[74] have shown that the parent imino triphenyl-phosphorane also reacted with a variety of carbonyl compound to afford the crossponding imines and triphenylphosphine oxide.

Appel[71], Bergmann[74]and Horner[85] have found the reaction of other N-substituted iminotriphenylphosphoranes with carbonyl compounds to produce analogous results.

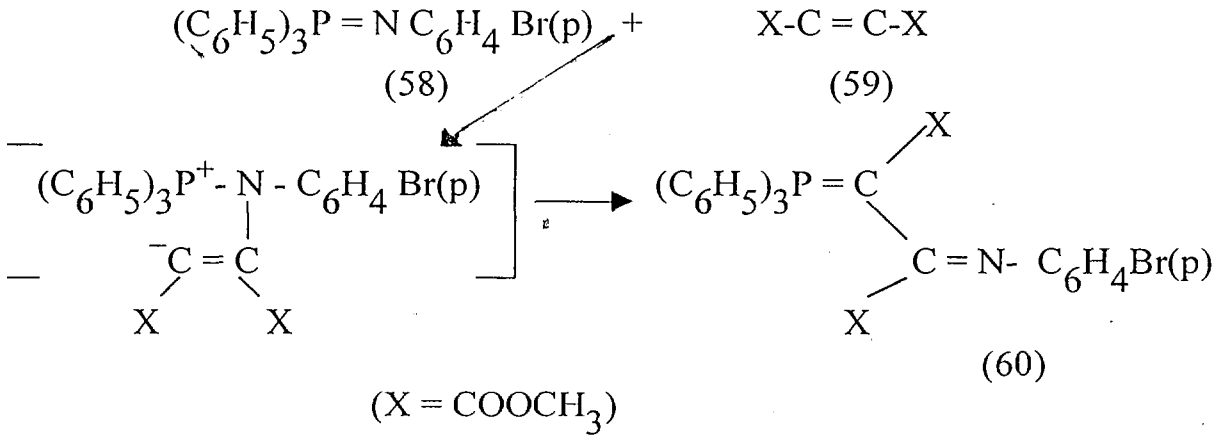
There have been no mechanistic studies on the reaction between carbonyl compounds and iminophosphoranes. It is likely that the mechanism will parallel rather closely the mechanism of the Wittig reaction between methylene phosphoranes and carbonyl compouds as shown below :

$$\begin{array}{l} R''_3\ P = N\text{-}\ R' \\ \quad + \\ R_2\ CO \end{array} \longrightarrow \left[\begin{array}{c} R''_3\ P^+ \text{-}\ N\ \text{-}\ R' \\ \quad\quad | \\ O^- \text{-}\ C\ \text{-}\ R \\ \quad\quad | \\ \quad\quad R \end{array} \right] \longrightarrow \begin{array}{l} R''_3\ PO \\ \quad + \\ R_2\ C = N\ \text{-}\ R' \end{array}$$

The First step should be betaine formation via nucleophilic attack of the nitrogen on the carbonyl carbon. This step could be reversible or irreversible. The second step should be the transfer of oxygen from carbon to phosphorous and it could be either reversible or irreversible.

The reaction between iminophosphoranes and dimethyl acetyle dicarboxalate (59) provides another illustration of the nucleophiliicity of the iminophosphorane operating in conjuction with the valence shell-expanding ability of the phosphorous atom there in. Brown[93] reported that (59) and N-phenylimino triphenyl phosphorane (56) afforded a 1:1 adduct that had a dipole moment of 5.3D and formed salts with hydrogen bromide and perchloric

acid similar adduct . were formed with the p-bromoisomer 56(58) and with the parent iminotriphenyl phosphorane (55). However, iminophosphorane carrying electron-withdrawing groups on nitrogen, those such as 2,4 dinitrophenyl, carbethoxy, benzoyl and p-toluenesulphonyl, all failed to react with (59), persumably because of their reduced nucleophilicity. The strucutre of the p-bromo adduct (60) was determined by X-ray crystallographic analysis[94] . The mechanism of the formation of the adducts probably involved the nucleophilic addition of the phosphine imine to the triple bond followed by phosphorous transfer from nitrogen to carbon. This last step would involve the formation of a pentavalent phosphorous atom in the transition state but would be quite analogous to the betaine decomposition step of the Wittig reaction.

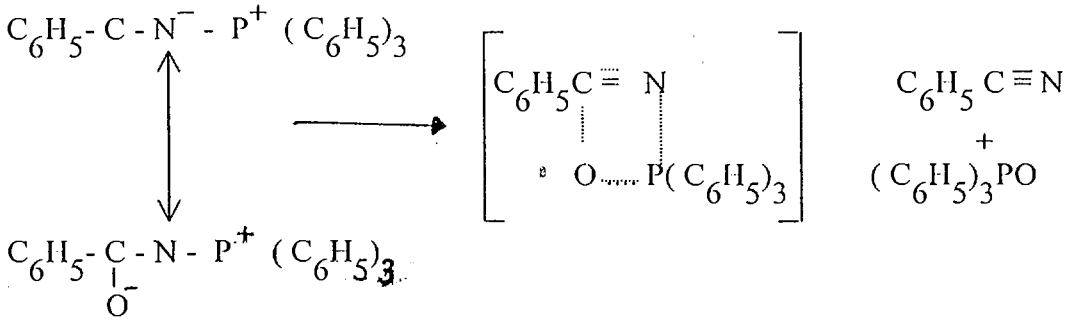


The overall result of the reaction is to convert an iminophosphorane into a methylenephosphorane but it is not clear what the driving force of this reaction might be. The situation is especially confusing when it is recalled that Bestmann and seng[81] reported the reverse transformationof a methylenephosphorane into an iminophosphorane by reaction with benzylidene aniline.

$$C_6H_5.CH\text{-}P(C_6H_5)_3 + C_6H_5.CH{=}N.C_6H_5 \longrightarrow C_6H_5.N = P(C_6H_5)_3 + C_6H_5CH = CHC_6H_5$$

$$(C_6H_5)_3P = N\,C_6H_5 \equiv X.C + C.X \longrightarrow (C_6H_5)_3\,P = C(X) - C(X) - NC_6H_5$$

Pyrolysis of N-acylimino triphenylphosphoranes proceeds in a manner analogous to that for ethylmethylene triphenylphosphorane which afforded alkynes and phosphine oxides. Staudinger and Hauser[78] reported the pyrolysis of N-benzoyl iminotriphenyl phosphorane (61) to afford benzonitrile and triphenyl phosphine oxide. The reaction probably involved a four-membered transition state for transfer of oxygen from carbon to phosphorous.



(61)

Horner and Gross[85] reported the same behaviour of the thiono analog of(61) and campbell[95] detected benzonitrite in the phospholene-catolyzed dimerization of benzoyl isocyanate which according to the proposed mechanism, should involve the intermediarty of[61]. Latter work by this group, however, indicated that the benzonitrite may arise from another source[96].

Trippett and Walker[97] reported the conversion of N-bromobenzamide into benzonitrite and triphenylphosphine oxide in the precence of triphenyl phosphine but claimed the reaction did not involve the intermediarcy of a phosphinimine[61] because of the mild conditions employed (mixing in benzene at room temperature).

1.2.4 Photochemical Reactions of Iminophosphoranes :

The irradiation of N-aryltriphenyliminophosphoranes in inert solvents leads to efficient production of triphenylphosphine and the diaryl azo compounds derived from the N-aryl ylid substituent. The irradiation of N-alkyltriphenyliminophosphoranes leads to rearrangements of the N-akyl

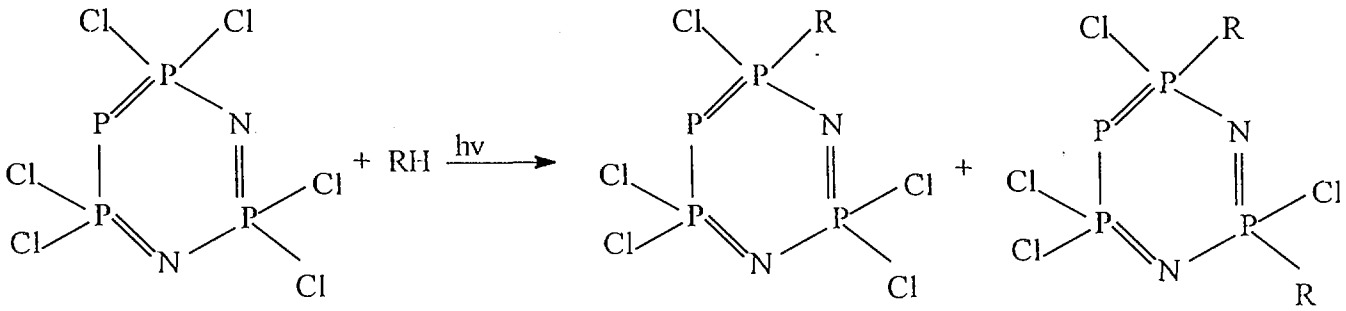
substitutent analogous to those observed during the irradiation of the corresponding azides triphenyl iminiophosphoranes which possess N-substituents capital of strong delocalization of nitrogen lone pair (e.g. benzene sulphonyl, benzoyl) are photostable. Since all attempts to trap nitrene intermediate suspected to be formed during the photoreaction of the photostable iminiophosphoranes were unsuccessful, the reaction are considered to proceed via excited yild intermediates[98].

Many ylids are susceptible to photolytic fragmention of the ylid bond. In theory homolytic dissociation of the heteromultiple bonds of the phosphorous-carbon, phosphorous-nitrogen, and analogous sulphur ylids can lead to stable phosphorous and sulphur derivatives and carbene or nitrene species.

$$R_nX = YR_m \xrightarrow{hv} R_nX : : YR_m$$

Most of the evidence for the intervention of carbene and nitrene intermediates in the photoreaction of P = C[99], S = C[100], and S = N[102] ylids comes from comparisons of the products formed in such reaction with those formed when these reactive intermediates are generated by alternate routes.

The relatively few investigation of photoreaction of phosphorous-nitrogen ylids have revealed that a variety of reaction are possible. Irradiation of cycloiminophosphoranes in hydrocarbon solvents results in low yield of the organosubstituted derivatives as the ony characterisable products[103].



CHAPTER TWO

2. EXPERIMENTAL DETAIL

Extremely Dry "or super dry' Ethyl Alcohol[103]

Clean dry magnesium turnings (5.0 gr) and iodine crystals (o.5 gr) were placed in a dry 2 litre round bottomed flask fitted with a double surface condenser and a drying tube, followed by (70 ml) of the 99% ethyl alcohol The mixture was warmed until the iodine had disappeared. Heating was continued until all the magnesium was converted into the ethylate. The absolute alcohol (900ml) were then added and the mixture was refluxed for 30 minutes. The alcohol was distilled off directly into the vessel in which it was to be stored.

Purification of Benzene[105] :

Benzene (1.0L) was added to sodium metal (5.0gr) which was out into small piecies and refluxed for 1 hour, then the solvent was distilled and stored in a dry vessel.

Purification of Nitrogen gas[106] :

The nitrogen gas was passed through an alkaline solution of pyrogallol (pyrogallol (15.0 gr) dissolved in soduim hydroxide solution 50% (100ml)) to remoe the traces of oxygen which the gas may contain. Then passed through a trap of anhydrous calcium chloride, then to the reaction vessel.

Preparation of Sodium Ethoxide[107] :

A suspension of granulated sodium (11.5 gr, 0.5 mol) in dry xylene was transfered to three necked flack (1.0L) and the xylene was decanted The sodium was washed by decantation with two portions of dry ether (20 ml) and covered with dry ether (200 ml) The flask was heated on a water bath and fitted with a mechanical stirrer, a reflux condenser and a dropping funnel, each protected by a calcium chloride guard tube. Absolute ethanol (29 ml, 0.5 mol) was run from the dropping funnel during 2 hours with gentle refluxing, and the mixture was continued reflexing with stirring until nearly all of the sodium had

reacted. The stirring stoped, the condenser was setted for downward distillation the ether was distlled off.. The white residue of sodium ethoxide was obtained.

Preparation of 2,4 - Dinitrobenzaldehyde[108, 109] :

Technical dimethylaniline (31.5 ml) in concentrated hydrochloric acid (105ml) were dissolved in 600 ml beaker, and finely crushed ice was added until the temperature fallen below 5°C . The contents of sodium nitrite (180gr) in water (30ml) were added slowly from a separatory funnel, the stem of which was dipped beneath the surface of the liquid. The temperature was maintained below 8°C by the addition of ice. When all the nitrite solution had been added the mixture was allowed to stand for one hour. A yellow crystalline solid was filtered, washed with dilute hydrochloric acid (1:1) (40 ml) and drained well then washed with little alcohol giving p-nitrosodimethyl aniline hydrochloride (36.0 gr, 77%).

p-Nitrosodimethyl aniline hydrochloride (15.0 gr) were transfered in 250 ml separatory funnel, water (50 ml) was added and shaken until a thin paste of uniform consistency was obtained. Aqueous sodium hydroxide solution(10%) was added with shaking until the whole mass had become bright green (the colour of the free base) and the mixture had an alkaline reaction. The free base was extracted by shaken with two portions of benzene (60 ml). The combined benzene extracts were dried with a little an hydrous potassium carbonate, filtered, and half of the benzene was distilled off. The residual hot benzene solution was poured in a beaker. Upon cooling the solid was crystallized in deep green leaflets, filtred and dried in air giving p-nitrosodimethyl aniline (13.0 g)

Dinitrotoluene (14.7g), p-nitrosodimethylaniline (13.0g) and sodium carbonate (1.5 gr) were condensed in boiling alcohol (75ml) for 5 hours giving dinitrobenzylidene p-aminodimenthylaniline (15.5 gr, 61.8%).

The crude material of dinitrobenzylidene-p-aminodimethlaniline (15.3gr) was covered with hydrochloric acid [concentrated HCl (19ml) and water (19ml)]. The mixture was boiled and steam being introduced to ensure vigorous agitation after 3-5 minutes at the boiling point. The whole was cooled. The aqueous liquor reomved and the solid remelted as before under a fresh portion of the same acid. The solid product was finally washed with water dried and recrystallized from hexane giving 2,4 - dinitrobenzaldehyde (7.0 gr, 72%) m.p 71°C (lit 72°C).

Preparation of o-Aminobenzophenone[114] (62) :

In a 5-litre three necked flask equipped with a stirrer and a thermometer extending to the bottom of the flask; water (1.5L) and technical grade dry sodium carbonate (260 gr, 2.4mol) were placed. While the mixture was warmed anthranilic acid (137 gr, 1.0 mol) was added in three portions, and the temperature was raised to 70° to effect complete solution. The solution was allowed to cool to about 60°C, and p-toluene sulphonyl chloride (230 gr, 1.2 mol) was added in five portions over a period of about 20 minutes. When all the p-toluene sulphonyl chloride had been added, the reaction mixture was maintained at 60°C for an additional 20 minutes. The temperature was raised to about 85°. Norite (10 gr) was added caustiously and the solution was filtered by suction through a previously heated Buchnr funnel.

In 4- litre beaker equipped with a stirrer which can be operate above the liquid level to break the foam, hydrochloric acid (12N) (250 ml) and water (250 ml) were placed. The filterate obtained above was cooled to about 50°C and added to the hydrochloric acid in a small portions at such a rate that the mixture did not foam over.

The product was isolated by filtration through a Buchner funnel and was washed on the filter, first with dilute hydrochloric acid (250ml) (prepared by diluting 50 ml hydrochloric acid to 250 ml). To remove anthranilic acid, and then with water (500ml). The product sucked as dry as possible and then

spreaded in a thin layer and allowed to air dry for about 15 hours, when easily pulverizable, the material was transfered to an oven and dried for 3 hours at 120°C. There was obtained a pale lavender poweder of p-toluenesulphonylanthranilic acid (25.7 gr, 88%) a netural equialent 294.

In a dry 3-litre necked flask equipped with a stirrer, a reflux condenser connected to a hydrogen chloride trap, and a thermometer extending to the bottom of the flask dry p-toluenesulphonylanthranitlic acid (164 gr, 0.5 mol), benzene (10.L) and phosphorous pentachloride (119 gr, 0.57mol) were placed. The mixture was stirred and heated at about 50°C for 30 minutes. The murky solution was then cooled to about 25°C and anhydrous aluminum chloride (290 gr, 2.2mol) was added in four portions. When the addition was completed, the dark mixture was heated with stirring at 80°C for 4 hours. The mixture was cooled to room temperature and poured on to a mixture of ice (500 gr) and hydrochloric acid (12N) (40ml) in a 5-litre round bottomed flask. The benzene was removed by vaccum distillation. The grainy, brown, crude product was separated by filtration on a Buchner funnel and washed throughly with dilute hydrochloric acid, with water, then with two portiond sodium carbonate 5% (500 ml) and finally with three portions water. The filtered cake was sucked reasonably dry.

The crude, moist sulphonamide was dissolved in concentrated sulphuric acid (1.5 l) by warming on the steam bath for 15 minutes. The sulphuric acid solution was devided into two equal parts, each of which was placed in a 4-litre beaker. The beakers was cooled in ice-bath while an ice (1.6 kg) was added slowly with stirring to the contents of each beaker. During the addition of ice, phenyl-p-tohylsuphone separates. Norite (50 gr) was added, and the solution was filtered. The filtrate was poured in to 5-gal croks half filled with crushed ice, then commercial ammonium hydroxide was added slowly with stirring. The solid was collected on a Buchner funnel, washed with water and then air dried. The product was obtained in the form of bright yellow crystals, recrystallized from hot ethanol (53 gr, 54%) m.p. 103-105°C (lit 105°C).

Preparationof o-Benzophenone Azide [111,112]:-

o-Aminobenzophenone (6.6gr,0.03mol) was dissolved in hydrochloric acid 20% (30 ml) and the mixture was warmed while stirring with magnetic stirrer until it dissolved forming o-aminobenzophenone chloride, then cooled to about 5°C. Sodium nitrite (2.5 gr, 0.03 mol) in water (25 ml) was added dropwise. After the addition was completed, it was stirred at 0°C for additional half an hour then a solution of sodium azide (1.95gr, 0.03mol) was added to the diazonium salt at 0°C dropwise, evolution of nitrogen gas start instanstously, after the addition was completed, it was left over night, extracted with ether, the ether died over an hydrous magnesium sulphate, then evaporated under reduced pressure. The oily azide was collected (5.8 gr, 82%).

Preparation Of Triphenylphosphine-o-benzophenonimine[98] (63) :

o-Benzophenone azide (5.8gr, 0.02 mol) in dry benzene (30 ml) was stirred while triphenylphosphine (6.5 gr, 0.026 mol) in dry benzene (30 ml) was added dropwise, evolution of nitrogen started after a while, then left stirrign over night, the solvent evaporated under reduced pressure light yellow solid was obtained, recrystallized from hot bnezene (10.65gr, 88%) m.p 176 - 178°C.

(Found : C, 8.85%, H, 5.29%, M (Mass spec)), 457, C_{31} H_{24} O N P requires, C, 81.40%, H, 5.28%, M, 457

Reaction Of Triphenyl phosphine-o-benzophenonimine With Benzaldehyde :

Benzaldehyde (0.3 gr) in dry benzene (10 ml) was added drop wise to triphenyl phosphine-o-benzophenonimine (1.3 gr) in dry benzene (20 ml). The mixture was refluxed for 20 hours. Monitored by TLC, no product was detected.

Reaction Of Triphenylphosphine-o-benzophenonimine With p-Nitrobenzaldehyde :

p-Nitrobenzaldehyde (0.35gr) in dry benzene (10 ml) was added dropwise to triphenylphosphine-o-benzophenonimine (1.1 gr) in dry benzene (20 ml). The mixture was refluxed for 15 hours , Monitored by TLC no product was detected.

Reaction Of Triphenylphosphine-o-benzophenonimine With 2,4-Dinitro benzaldehyde :

2,4-Dinitrobenzaldehyde (0.2 gr) in dry benzene (5 ml) was added to triphenylphosphine-o-benzophenonimine (0.45 gr) in dry benezene (10 ml), refluxed for 10 hours. Monintored by TLC no product was detected.

Irradiation Of Triphenylphosphine-o-benzophenonimine[113] (63) :

Triphenylphosphine-o-benzphenonimine (63) (2.0gr) in dry bnezene (250 ml) purged with nitrogen gas was irradiated for 13 hours using Hanoia medium pressure uv immersion lamp The reaction mixture was concentrated to about 10 ml and monitored by TLC. No reaction was detected.

Preparation Of p-Benzophenone Azide[111, 112] :-

p.Aminobenzophenone (3.2 gr, 0.01mol) in sulphuric acid 20% (40ml) was heated while stirring with mechanical stirrer until it dissolved, then cooled in ice-bath to below 5°C, sodium nitrite (1.3gr, 0.01mol) was dissolved in water (15ml) and cooled below 5°C, then added dropwise to the stirred a mine salt solution. After addition was compeleted it left half an hour stirring in the ice-bath. A solution of sodium azide (1.2 gr, 0.01 mol) in water (15 ml) was added dropwise to the cold diazonium salt. The solution stirred for 3 hours monitored by TLC, then filtered and washed with water giving white yellow crystal (3.0 gr, 83%) m.p. 61°C.

Preparation Of Triphenyl phosphine-p-benzophenonimine [98](64)

Triphenyphosphine (2.6gr, 0.01 mol) in dry benzene (25ml) was added dropwise to a solution of p-benzophenone azide (2.23gr, 0.01mol) in dry benzene (20ml) while stirring. Reaction started after addition of few ml of triphenylphosphine solution and nitrogen started to evolve vigrously. The solution left stirring overnight, then the solvent distilled under reduced pressure and the residue was crystallized from benzene/pet-ether (3.0gr, 65%)m.p. 105 - 106°C.

(Found : C, 8.85%, H, 5.29%%, M (Mass spec)), 457, C_{31} H_{24} O N P requires, C, 81.40%, H, 5.28%, M, 457.

Reaction Of Triphenylphosphine-p-benzophenonimine With Benzaddehyde :

Benzaldehyde (0.3gr) in dry benzene (10 ml) was added dropwise to triphenylphosphine-p-benzophenonimine (1.3 gr) in dry benzene (20 ml) the mixture was refluxed for 15 hours. Monitored by TLC no reaction was detected.

Reaction Of Triphenylphosphine-p-benzophenonimine With p-Nitrobenzaldehyde :

p-Nitrobenzaldehyde (0.35gr) in dry benzene (10ml) was added dropwise to triphenylphospine-p-benzonphenonimine (1.1gr) in dry benzene (20ml). The mixture was refluxed for 10 hours, Monitored by TLC no reaction was detected.

Reaction Of Triphenylphosphine-p-benzophenonimine With 2,4-Dinitrobenzaldelyde :

2,4-Dinitrobenzaldehyde (0.2 gr) in dry benzene (5 ml) was added to triphennylphospine-p-benzophenonimine (0.45gr) in dry benzene (10 ml) Refluxed for 10 hours, monitored by TLC, no reaction was detected.

Irradiation Of Triphenylphosphine-p-benzophenonimine (64) :

Triphenylphosphine-p-benzophenonimine (1.0 gr) in dry benzene (250ml) purged with nitrogen gas was irradiated for 20 hours using Hanovia medium pressure UV imersion lamp. The reaction mixture was concentrated to about 10 ml and monitored by TLC no reaction was detected.

Preparation o-Benzylaniline[114] :

In 500ml three-necked flask equipped with a separatory funnel, a mechanical stirrer and a reflux condenser, pure sodium bicarbonate (35gr), water (35ml) and aniline (121ml, 1.3 mole) were poured, the stirring was started, freshly distilled benzyl chloride (35ml, 0.3 mol) was added from the separatory funnel to the previously heated mixture (90 - 95°) dropwise (1 hour). The heating and stirring were continued for further 3 hours. The mixture was allowed to cool, then filtered with suction, the organic layer was separated and was washed with saturated salt solution (25 ml), dried over anhydrous magnesium sulphate and filtered again with suction and distilled under reduced pressure, the o-benzylaniline was collected (52 gr, 85%) m.p. 34°C (lit 35°C).

Preparation Of o-phenylbenzyl azide[111,112] :

o-Benzylaniline (1.8 gr, 0.01mol) in water 20 ml) dissolved in excess dilute hydrochloric acid (15 ml). This was warmed with stirring to ensure that all had dissolved. Then cooled in ice-bath to 0°C. Solution of sodium nitrite (0.75gr, 0.01 mol) in water (15 ml) was added to the stirred cold solutin dropwise. After the addition was completed it was stirred for half an hour at 0°C. Then filtrered cold and again put back in ice-bath and solution of sodium

azide (0.68gr, 0.01mol), evolution of nitrogen gas started instantously. After the addition was completed, it was extracted with ether, dried over anhydrous sodium sulphate, filtered and the ether evaporated under vaccum gave oil azide (1.8 gr, 89T)

Preparation Of Triphenyphosphine-o-phenylbenzylimine [98](65) :

o-phenyl azide (1.87gr, 0.008mol) was dessolved in dry benzene (10 ml). To this solution triphenylphosphine (2.33gr, 0.008mol) in dry benzene (15 ml) was added dropwise with stirring. Nitrogen evolution was not very much a parent, therefore; external heating was carried out. First with hot water, second refluxed for 2 hours. When the solvent takken off a dark gummy material remained, titurated with ethanol. Some material was taken with. A short column of silica gel was prepared and the solid was introudced on top. Elution started with chloroform / heaxane 5% (50 ml), then with 10%. Light yellow crystalls were collected (3.2 gr, 82%) m.p. 121-123°C.

(Found : C, 83.5%, H, 5.62%, M (Mass spect)), 443 C_{31} H_{26} N P requires, C, 83.76%, H, 5.89%, M, 443.

Reaction Of Triphenylphosphine-o-phenylbenzylimine With Benzaldehyde :

Benzaldehyde (0.3gr) in dry ethanol (10ml) was added to triphenylphosphine-o-phenylbenzylimine (1.4 gr) in dry ethanol (20ml). The mixture was refluxed for 15 hours. The reaction mixture was monotored by TLC no product was detected.

Reaction Of Triphenylphosphine-o-phenylbenzylimine With p-Nitrobenzaldehyde :

P-Nitrobenzaldehyde (1.5 gr) in dry ethanol (20ml) was added to triphenylphospine-o-phenylbenzylimine (0.4 gr) in dry ethanol (10ml). The

mixture was refluxed for 3 hours. When cooled the crystals of the product were separated and recrystallized from hot ethanol giving yellow crystals (0.3gr, 95%) m.p. 68°C.

Reaction Of Triphenylphosphine-o-phenylbenzylimine With 2,4-Dinitrobenzaldehyde :

2,4-Dinitrobenzaldehyde (0.2 gr) in dry ethanol (5ml) was added to tripheynlphosphine-o-phenylbenzylimine (0.4 gr) in dry yellow crystals was obtained (0.2 gr, 61%) m.p. 58°C.

Irradiation Of Triphenyl phosphine-o-phenylbenzylimine [113](65) :

Triphenylphosphine-o-phenylbenzylimine (2.0gr) in dyr benzene (250ml) purged with nitrogen gas was irradiated for 3 hours using Hanovia medium pressure UV immersion lamp. The reaction mixture was concentrated to about 10 ml.

A column of 50 cm (CR32/40) was prepared. The dry looking mixture of support plus stationary phase (silica gel 60 - 120 mesh for adsorption chromatographic analsis) (50.0 gr) was stirred with some of the mobile phase to be used (pet-ether (40-60) The slury was then poured in small portion in to the column which contained a little of the same solvent. Each portion of solid must be first throughly stirred up and then packed down with firm slow strokes, successive portions were well mixed with the top of the preceding portion to avoid striation. Excess solvent was allowed to run through the column. The sample was applied to the top of the column by a dropper-tube. When all the sample had been adsorbed on the top of the column the vacant space above it was filled with the solvent and the column allowed to run. Three fractions were collected and monitored by TLC.

Fraction (1) was identified as triphenyl phosphine m.p. 80°C Fraction (2) was o-azobenzylbenzene m.p. 117°C.

(Found : C, 86.29%, H, 6.21%, M (Mass sepct)), 362, $C_{26}H_{22}N_2$ requires, C, 86.15%, H, 6.11%, M, 362.

Prepartion Of o-Aminobenzophenone ethylene acetal [115](66) :

o-Aminobenzophenone (7.0 gr, 0.05 mol); ethylene glycol (4.0gr, 0.06 mol) and p-toluene sulphonic acid (0.2 gr) in dry benzene (100ml) were placed in (250ml) round bottomed flask fitted with a Dean and stark water separator and a reflux condenser. The mixture was refluxed for 12 hours until no more water was collected. Two additional quantities of ethylene glycol (4.0gr) were added during the reaction period. The resulting reaction mixture was concentrated, washed with two portions a queous sodium bicarbonate, extracted with ether and the ether evaporated under vaccum. Yellow crystals were collected. Recrystallized from hot benzene gave (6.0 gr, 70%) m.p. 185°-187°C.

Preparation Of Triphenylphosphinum-o-benzophenone ethylene acetal bromide[6] (67) :

Triphenylphosphine (2.6gr, 0.01 mol) in dry benzene (10ml) was placed in a three necked flask fitted with a mechanical stirrer, condenser and a dropping funnel at 0°C under nitrogen gas. Bromine (0.5ml, 0.01mol) was added dropwise. The stirring was continued after the addition was completed for half an hour. To this, a mixture of o-aminobenzophenone ethylene acetal (2.6 gr, 0.01 mol) and triethylamine (1.0ml, 0.01mol) were added dropwise while stirring. After the addition was completed, it was also stirred for half an hour, then filtered at suction pump and washed with ether, then quickly with cold water to remove triethylammonium bromide, then with ether. The remaining product was dried and recrystallized from hot ethanol gave (2.0gr, 33%) m.p. 200-201°C.

Preparation Of Triphenylphosphine-o-benzophenonimine-ethylene acetal (68) :

Triphenylphosphonium-o-benzophenoneethyleneacetalbromide (2.0gr, 0.003mol) was dissolved in dry ethanol (20ml) and sodium ethoxide (0.2 gr, 0.003 mol) was added dropwise during stirring. A fter the addition was completed the solvent distilled off and the crystals were collected, recrystallized from chloroform/pet-ether (1:1) a light brown crystals were obtained (1.5 gr, 88%) m.p. 158°C.

Reaction Of Triphenylphospine-o-benzophenonimine ethylene acetal With Benzaldehyde :-

Benzaldehyde (0.2 gr, 0.001 mol) in dry benzene (5ml) was added to triphenylphosine-o-benzophenonimine ethylene acetal (0.5 gr, 0,001 mol) in dry benzene (10ml) and the mixture was refluxed for 10 hours when the mixture cooled light crystals were collected (0.2gr, 76%) m.p 116°C.

Reaction Of Triphenylphosphine-o-benzophenonimine-ethylene acetal With p-Nitrobenaldehyde :

p-Nitrobenzaldehyde (0.2gr, 0.001mol); in dry benzene (10 ml) was added to triphenylphosphine-o-benzophenonimine ethylene acetal (0.5gr, 0.001) in dry benzene (10 ml) and refluxed for 3 hours. When cooled the crystals of the product separated and recrystallized from hot ethanol giving yellow crystals (o.2 gr, 66%) m.p 79-81°C.

Reaction Of Triphenylphosphine-o-benzophenonimine ethylene acetal With 2,4-Dinitrobenaldehyde :

2,4-Dinitrobenzaldehyde (0.2gr) in dry benzene (5ml) was added to triphenylphosphine-o-benzophenonimine ethylene acetal (0.4 gr) in dry benzene (10ml) and refluxed for 2 hours, when the reaction mixture was cooled a yellow cyrstals was obtained (0.3gr, 88%) m.p 106°C.

Irradiation Of Triphenylphosphine-o-benophenonimine ethylene acetal [113] (68) :

Triphenylphosphine-o-benzophenonimine ethylene acetal (1.0gr) in dry benezene (250ml) purged with nitrogen gas was irradiated for 12 hours using Hanovia medium pressure UV immersion lamp. The reaction mixture was concentrated to about 10 ml. Three fractions was collected and monitored by TLC

Fraction (1) was identified as triphenylphospine m.p. 80°C

Fraction (2) dark red crystals (o-ozobenzophenone ethylene acetal) m.p 140°C

Fraction (3) starting material m.p. 158°C.

Preparation Of m-Nitrobenzophenone [116] (69):

Method (1) :

In 500ml round bottomed flask, immersed in an ice-salt bath, concentrated sulphuric acid (75 ml) was placed, the flask was equipped with a mechanical stirrer, a small dropping funnel and a thermometer reaching almost to the bottom of the flask. The stirrer was started and when the sulphuric acid had cooled below 0°C a pure benzophenone (45gr, 0.25mol) was slowly added at such rate that the temperature did not rose above 5°C. After the reaction mixture had cooled to about -7°C, the cooled nitrating mixture (nitric acid (20ml) and concentrated sulphuric acid (30mol)) was added through the dropping funnel dropwise that the temperature of the reaction mixture remained at 0°C. After the nitrating acids had been added, stirring was continued for 10 minutes longer, then the contents of the flask were poured, with vigorous manual stirring into a mixture of crushed ice (350gr, and water (750ml). The product was seperated as a yellow flocculent solid.

After the ice had melted, the product was filtered by suction and sticky mass pressed as dry as possible, then it was transfered to mortar and titurated with three successive portions of water (150ml) then with two successive portion of ice-cold ethyl alcohol (25 ml), the solid was pressed dry on the suction filter after each of the five washings. The product was pressed on a porous plate and, when fairly dry it was dissolved in ethyl alcohol (50ml), the dark solution was quickly filtered and the hot filtrate was poured slowly into cold water (500ml) which was stirred vigorously. After standing a few minutes, the yellow solid was filtered, washed with water and air dried. Monotoring by TLC show many products.

Preparation Of m-Nitrobenzoyl chloride [117] :

The redistilled thionyl chloride (25ml, 0.2 mol) and m-nitrobenzoic acid (25gr, 0.2 mol were reluxed for 3 hours using a water bath and a condenser guarded with calcuim chloride tube. Then the excess thionyl chloride was distilled off. The product was distilled under reduced pressure and a pure m-nitrobenzoyl chloride was obtained (230 gr, 76%) m.p. 33°C (lit 33°C).

Preparation Of m-Nitrobenzophenone [118]:

Method (2) :

In 500 ml round bottomed flask a dry benzene (120 ml) and m-nitrobenzoyl chloride (23 gr) were placed. Finely powdered an hydrous aluminium chloride (30 gr) was added with frequent stirring during 30 minutes to the content of the flask. The mixture was refluxed for 3 hours using a condenser guarded with a hydrogen chloride trap until no longer hdyrogen chloride evolved, the content of the flask was poured while still warmed into a mixture of crushed ice (200 gr) and concentrated hydrochloric acid (100ml). The benzene layer was separated, washed with sodium hydroxide solution 5% (50ml), then with water and dried over an hydrous magnesium sulphate. The

benzene distilled off. A white precipitate was obtained, recrystallized from hot ethanol gave (20.0 gr, 77%) m.p 92°C (lit 94°C).

Preparation Of m-Aminobenzophenone[119] (70) :

Method (1)

In 250 ml round bottomed flask fitted with a reflux condenser, m-nitrobenzophenone (2.0 gr) and granulated tin (4.0 gr) were placed, concentrated hydrochloric acid (20 ml) was added in three equal portions to the mixture which was shaked throughly after each addition. When the vigorous reaction subsided, it was heated under reflux for half an hour. Then the mixture was cooled, sodium hydroxide solution 30% was added until the precipitate of tin hydroxide dissolved. The resulting a mine was extracted with ether and the ether distilled under reduced pressure; low yield was obtained.

Preparation Of m-Aminobenzophenone[120] :

Method (2) :

m-Nitrobenzophenone (5.0 gr) was dissolved in absolute ethanol (80ml); platinum oxide (0.2 gr) was added. The reaction mixture was hydrogenated with stirring at room temperature and atomspheric pressure. A fter a period of 5 hours, the theoretical up take of hydrogen was attained, the catalyst was filtered off and the filtrate was concentrated and crystallized from hot water giving almost yield (4.0gr, 93%) m.p. 86° (lit 87°C).

Preparation Of m-Benzophenone Azide[111,112] :

m-Aminobenzophenone (4.0 gr, 0.02 mol) in hydrochloric acid (30 ml) was stirred with mechanical stirrer, then cooled in ice-bath to below 5°C. Sodium nitrite (1.3 gr, 0.02 mol) in water (15 ml) and cooled below 5°C was added dropwise to the stirred amine salt solution. After the addition was completed, it was left to stirr for half an hour in the ice-bath. A solution of sodium azide (1.38 gr, 0.02 mol) in water (15 ml) was added dropwise to the

cooled diazonium salt. The solution stirred for 3 hours then extracted with ether, washed with sodium bicarbonate 5%, then twice with water. The ether dried over an hydrous sodium sulphate, the ether evaporated under vaccum, oily azide was obtained (3.5 gr, 77%).

Preparation Of Triphenyl phosphine-m-benzphenonimine[98](71) :

Triphenylphosphine (4.5 gr, 0.017 mol) in dry benzene (20 ml) was added dropwise at room temperature under an hydrous condition to m.benzohenoneazide (3.5 gr, 0.017 mol) in dry benzene (20 ml), Evolution of nitrogen occured after additin of few drops of triphenyl phosphine. The mixture was stirred over night, gummy material was obtained, recrystallized from hot benzene gave light crystals (5.0 gr, 83%) m.p. 162°C.

Reaction Of Triphenylphosphine-m-benzophenonimine With Benzaldehyde :

Benzaldehyde (0.3gr) in dry benzene (10ml) was added dropwise to triphenylphosphine-m-benzophenonimine (1.3gr) in dry benzene (20ml). The mixture was refluxed for 15 hours. Monitored by TLC. no product was detected.

Reaction Of Triphenylphosphine-m-benzophenonimine With p-Nitrobenzaldehyde :

p-Nitrobenzaldehyde (0.35gr) in dry benzene (10ml) was added dropwise to triphenylphosphine-m-benzophenonimine (1.1gr) in dry benzene. The mixture was refluxed for 3 hours. When cooled the crystals of the product were separated and recrystallized from ethanal gave yellow crystals (0.6 gr, 75%) m.p 82°C.

Reaction Of Triphenylphosphine-m-benzophenonimine With 2,4-Dinitrobenzaldehyde :

2,4-Dinitrobenzaldehyde (0.2gr) in dry benzene (5ml) was added dropwise to triphenylphosphine-m-benzophenonimine (0.45 gr) in dry benzene. Refluxed for 1 hour. When cooled light crystals was obtained (0.3gr, 81%) m.p. 66°C.

Irradiation Of Triphenylphosphine-m-benzophenonimine (73) :

Triphenylphosphine-m-benzophenonimine (2.0gr) in dry benzene (250ml) purged with nitrogen gas was irradiated for 6 hours using Hanovia medium pressure UV lamp. The reaction mixture was concentrated to about 10 ml. Three fractions were collected and monitored by TLC.

Fraction (1) was identified as triphenylphosphine m.p. 80°C.

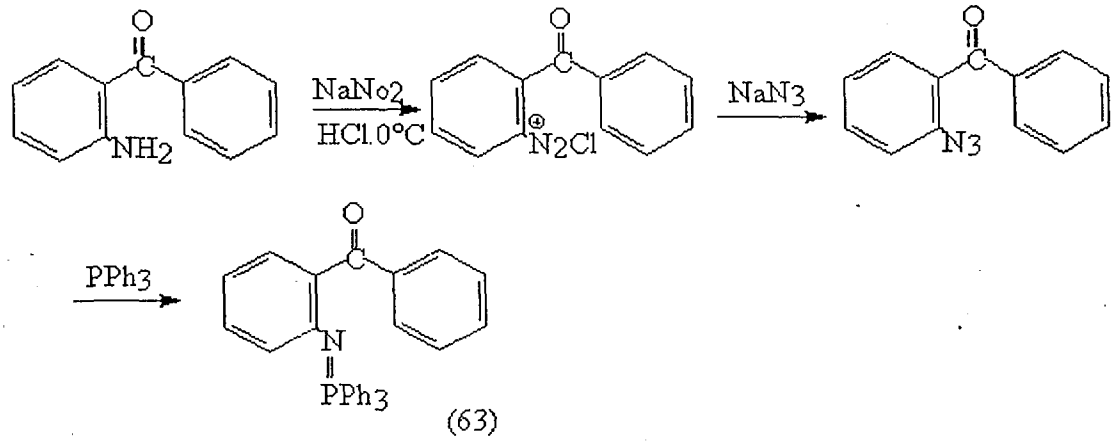
Fraction (2) yellow crystals m.p. 152°C.

CHAPTER THREE

3. RESULT AN DISCUSSION

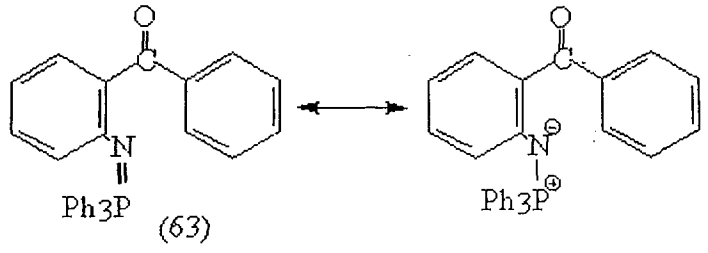
3.1 Reaction of Triphenylphosphine-o-benzophenonimine (63) :

Triphenylphosphine-o-benzophenonimine (63) was prepared by diazotization of o-aminobenzophenone, then treated with a solution of sodium azide. The azide formed, dissolved in benzene and reacted with a solution of triphenylphosphine in benezene to give the desired product in good yield.



Scheme (1) : Route employed for preparation of Triphenylphosphine-o-benzophenonimine.

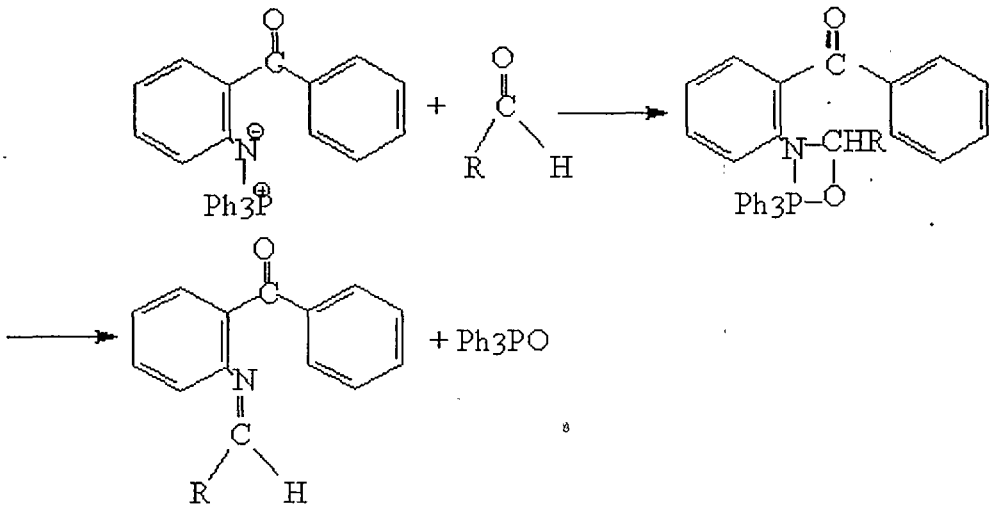
Triphenylphosphine-o-benzophenonimine is expected to react in a



similar manner to other phosphinimines (Wittig type of reation)[6].

The familiar resonance of Pπ - dπ bond of the phosphinimine where the more electronegative nitrogen atom aquires the negative charge and phosphorous the positive charge. Thus it is expected that the generated nucleophile can attack carbon atom of carbonyl groups of aldehydes and ketones. However, when it was reacted with different aldehyde namely benzaldehyde p-nitrobenzalehyde and 2,4-dinitorbenzaldehyde, no reaction

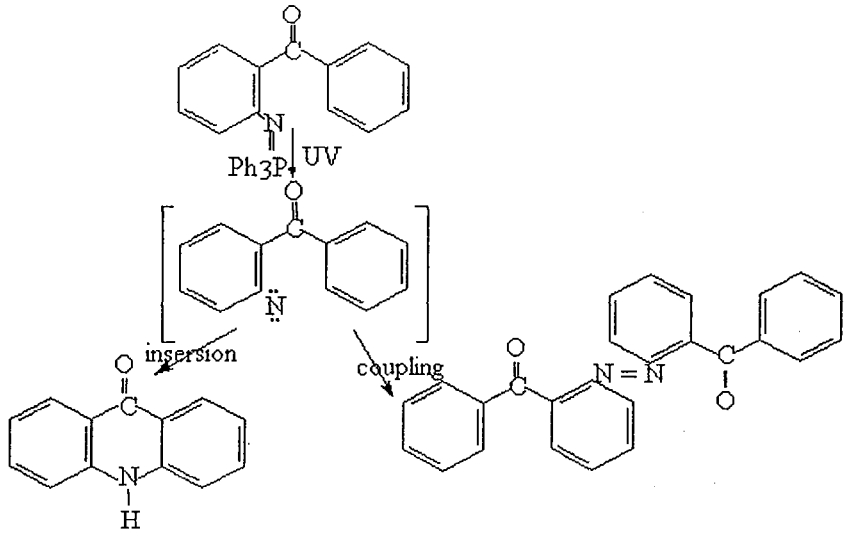
took place and the starting material was recovered in each case. This was rather surprising result.



Scheme (2) The expected reaction that never took place.

3.1.1 The Photolysis of Triphenylphosphine-o-benzo-phenonimine (63) :

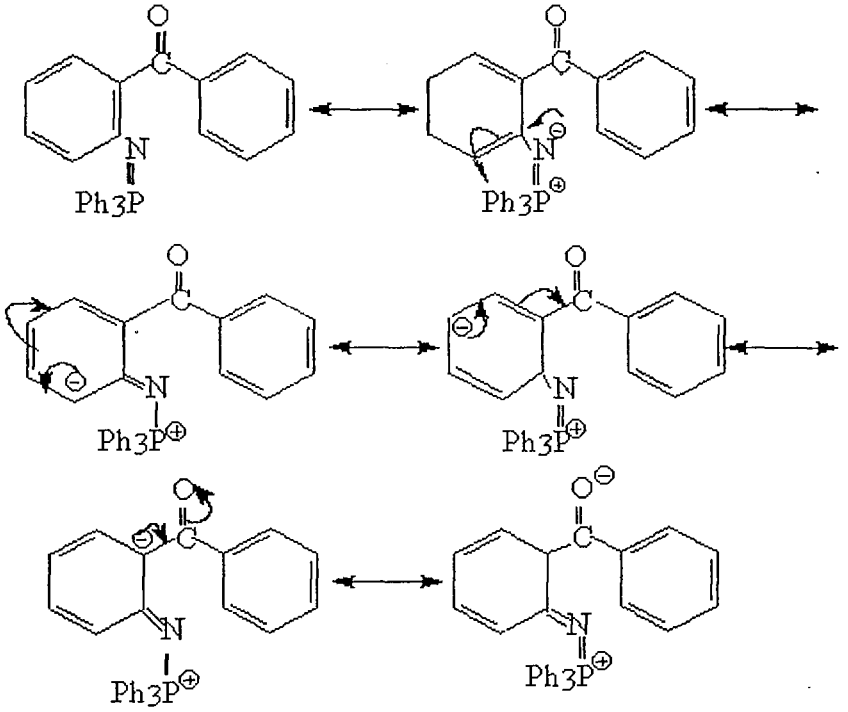
Triphenylphosphine-o-benzophenonimine in dry benzene was irradiated after purged with oxygen free nitrogen gas, using Hanovia medium pressure UV lamp of immersion well type. Starting material was recovered after more than 12 hours irradiation.



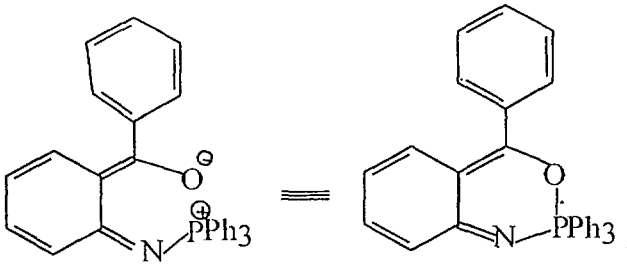
Scheme (3) Show so the expected products of the photochemical reaction of triphenylphosphine-o-benzophenonimine.

It is clear that both reactions, chemical and photochemical, did not take place. Thus triphenylphosphine-o-benzophenonimine (63) is very unreactive and that means that the $\rangle P = N$ - bond could not be broken to give products in one hand, and on the other hand that the nucleophilicity of nitrogen is very weak to attack carbonyl carbons.

This could well be explained if we look at the resonance structures of the compound.



The last resonance form can be better seen in the following manner.

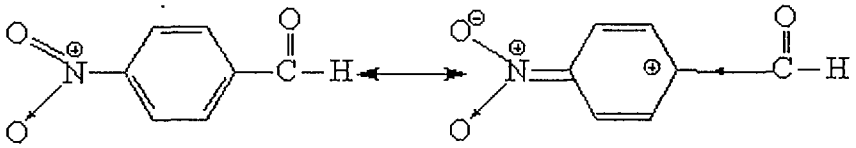


(63a)

Strucutre (63a) is an unstrained six membered ring. Triphenylphosphine-o-benzophenonimine (63), as shown, could exist in eight contributing resonance forms. However, only one strucutre out of the eight had the negative

charge on the nitrogen atom, thus making this nitrogen almost non-nucleophilic. This could well explain its unreactivity toword Wittig type of reactions which depend on nucleophilicity of the nitrogen as well as the electrophilicity of the substrate, the carbonyl carbon.

In our reactions with different aldehydes we increased their electrophilicity by introducing nitro-groups which are known as powerfull eclectron withdrowing groups.

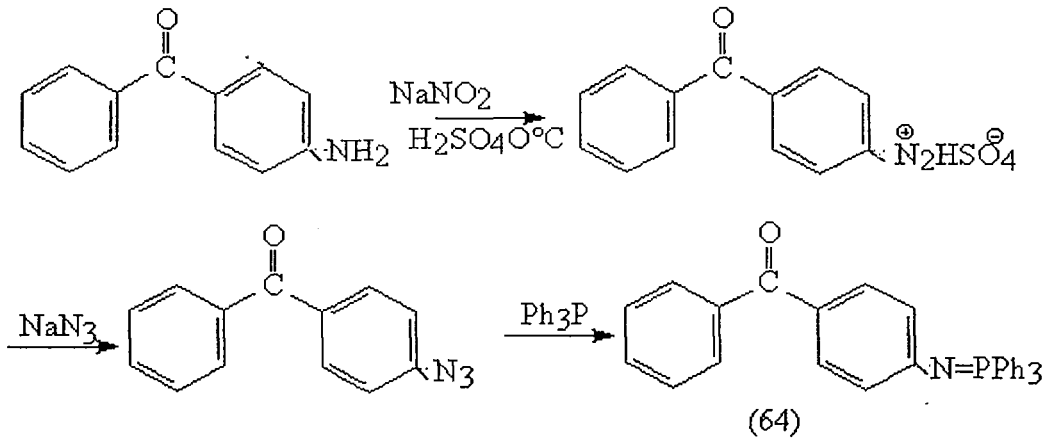


When the nitro group is placed ortho or para, it operates by both inductive effect and resonance effect as shown above where the positive charge is place on the carbon bearing the aldehydic group. This increases the positive character of the carbonyl carbon.

By placing two nitro groups as in the 2,4-dinitrobenzaldehydes the electrophilicity is increased tremendously. This should have helped even weak nucleophililes to attack, but as mentioned above it did not happen with triphenylphosphine-o-benzophenonimine (63) stressing the point of its inertness as a nucleophile

3.2 Reaction of Triphenylphosphine-p-benzophenonimine (64) :

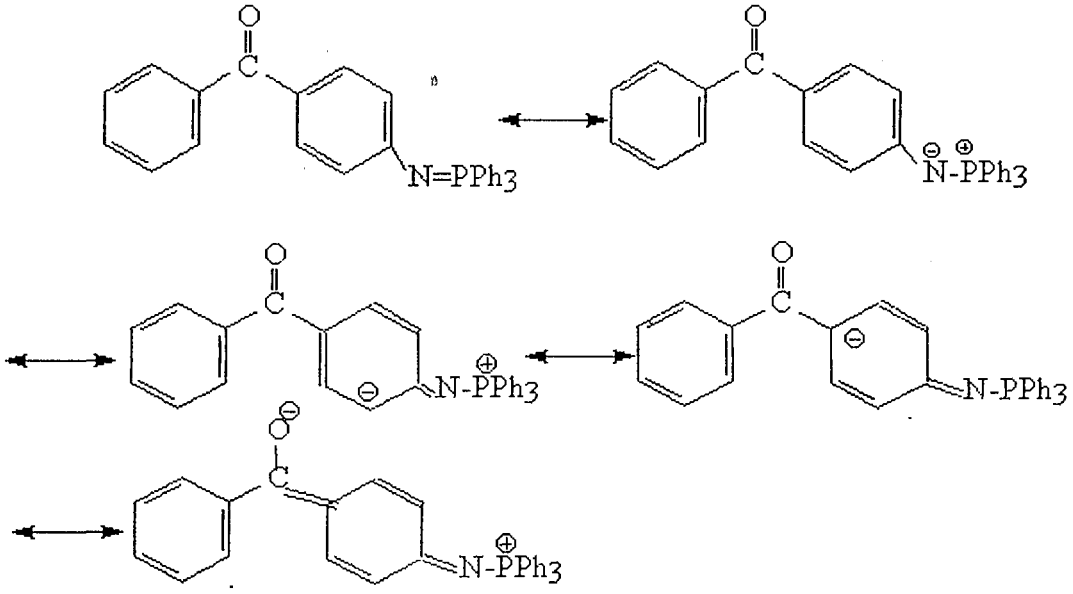
Triphenylphosphine-p-benzophnonimine (64) was prepared by diazotization of p-aminobenzophenone, then treated with a solution of sodium azide. The azide formed dissolved in benzene and reacted with a solution of triphenylphosphine in benzene to give the desired product in good yield.



(64)

Scheme (4) Route employed for the preparation of triphenylphosphine-p-benzophenonimine

Triphenylphosphine-p-benzophenonimine (64) was reacted with benzaldehydes and its nitro substitutents. It failed to react with none of them and this is due to direct conjugation of the negative charge on the nitrogen with the carbonyl group.



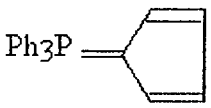
The contributing resonance structure of triphenylphosphine-p-benzophenonimine showed that also out of five resonance structures only one with the negative charge on nitrogen atom. This dispersion of electrons (of the negative charge) away from nitrogen atom to oxygen atom is more favourable. This because oxygen is more electronegative than the nitrogen, therefore; it

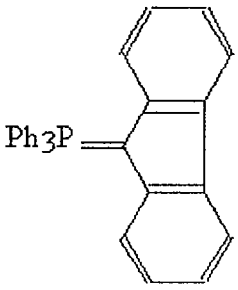
accomodates the electrons better. This also explains unreactivity of the para isomer chemically and photochemically.

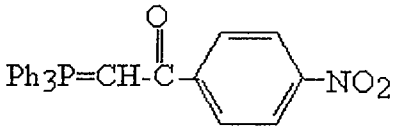
3.2.1 The Photolysis of Triphenylphosphine-p-benzo-phenonimine (64) :

Triphenylphosphine-p-benzophenonimine was irradiated for 20 hours using Hanovia medium pressure UV lamp. The reaction mixture was concentrated and monitored by TLC but no product was detected. This as explained above due to great stability of the compound.

Many stable Wittig reagents were reported[121]. Such highly un reactive compounds were found to have strong conjugation. The following are examples of such phosphoranes :

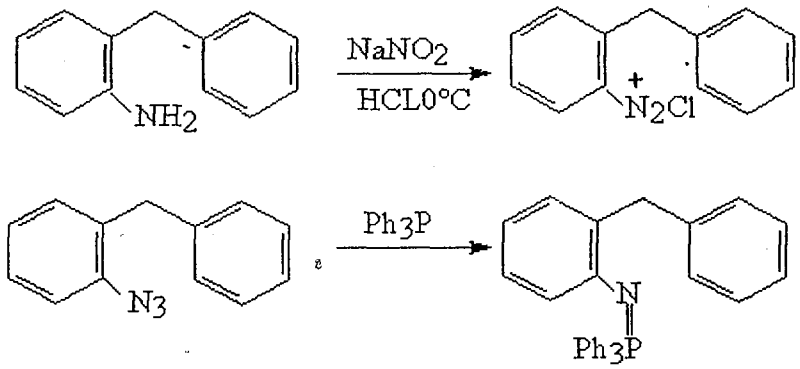






3.3 The Reaction of Triphenylphosphine-o-benzylphenylimine (65) :

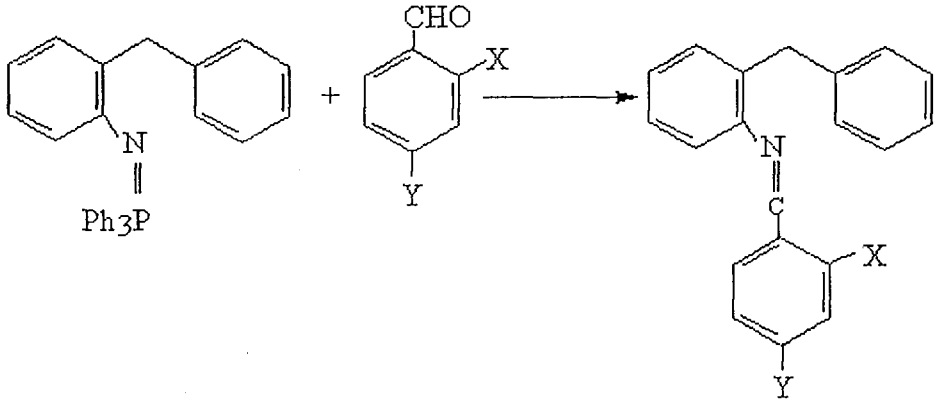
Triphenylphosphine-o-benzylphenylmine (65) was prepared by diazotization of o-benzylaniline and then treated with aqueous sodium azide. The azide formed, dissolved in benzene was reacted with a solution of triphenylphosphine in benzene which gave the desired product in good yields



(65)

Scheme (5) Route employed for the preparation of triphenylphosphine-o-benzylphenylimine

Triphenylphosphine-o-benzylphenylimine was reacted sepearately with benzaldehyde, p-nitrobenzaldehyde and 2,4-dinitrobenzaldehyde. With benzaldehyde it failed to react, however, it did with p-nitrobenzaldehyde and also with 2,4-dinitrobenzaldehyde giving the corresponding schiff's bases.



(65a) : X = H, Y = No_2

(65b) : X = No_2, Y = No_2

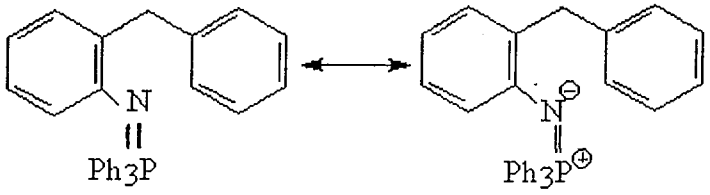
Scheme (6) Reaction of Triphenylphosphine-o-benzylphenylimine with nitro-substituted benaldehyde.

This reaction is a nucleophilic attack by the nitrogen of the triphenylphospine-o-benzylphenylimine and the carbon atom of the aldehyde

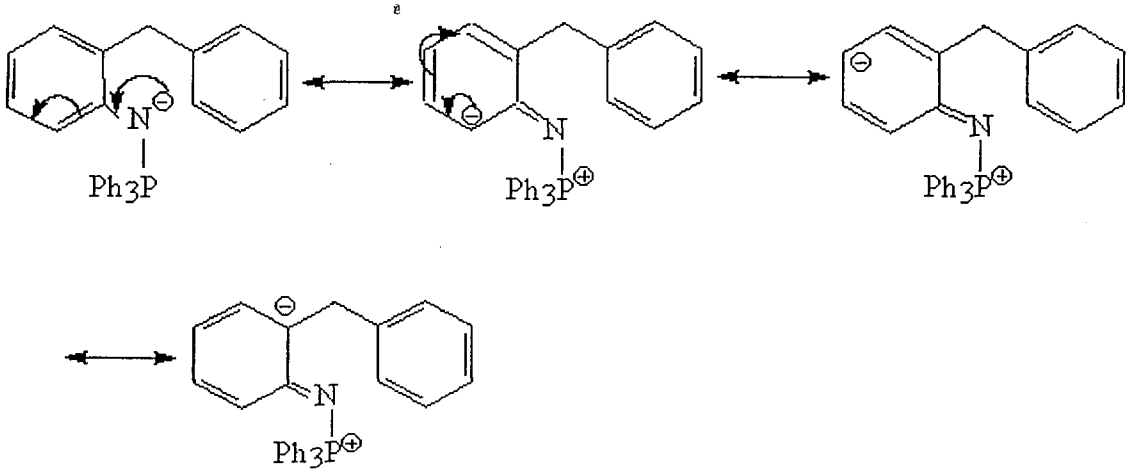
carbonyl group therefore; for the reaction to occur the nucleophilicity of the nuclephile and the positive character (electrophilicity) on the substrate are very important factors. If both are strong the reaction will be favourable and faster. On the other hand, if both are weak the reaction might not take place at all. Thus the reaction with benzaldehyde did not occur because of the relative low nucleophilicity of the triphenylphosphine-o-benzylphenylimine (however it is strong nucleophile when we compared it with triphenylphosphine-o-benzophenonimine and triphenylphosphine-p-benzopheno-nimine) in addition to the relative low electrophilicity of the carbonyl carbon of benzaldehyde.

On the other hand it reacts with p-nitrobenzaldehyde and 2,4-dinitrobenzaldehyde because their electrophilicity was increased by introducing the nitro and dinitro-groups respectively.

It has always been known that phosphorous ylids exist in resonance forms because of the polarity of the phosphorous-nitrogen double bond (dπ-pπ)



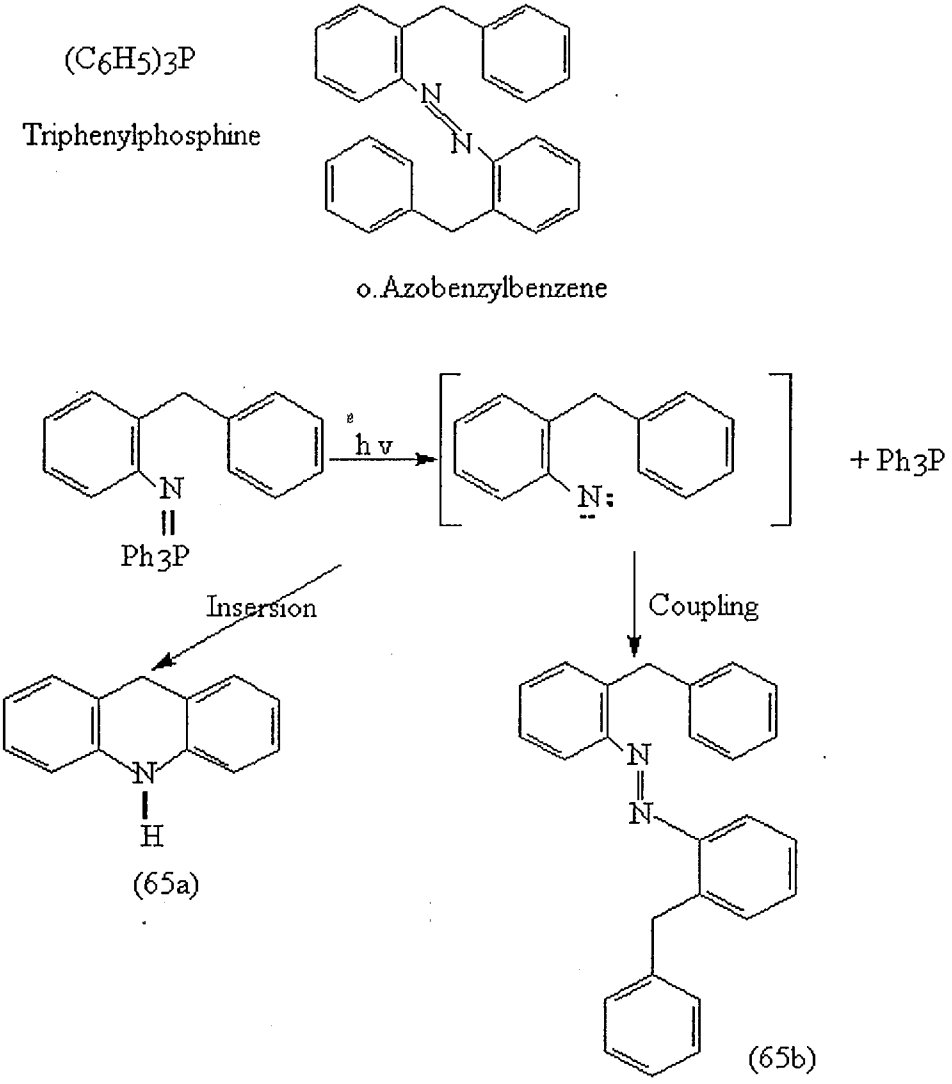
The negative charged nitrogen been in conjugation with a π-system of the phenyl group. Thus delocalization occurs giving four different resonance forms as illustrated below.



This delocalizaiton of the negative charge on the nitrogen ultimately decreases its nucleophilicity, thus decreases its reactivity except with carbonyl groups with strong positive character. That is why it did not react with benzaldehyde but it did with p-nitrobenzaldehyde and 2,4-dinitrobenzal-dehyde.

3.3.1 The Photolysis of Triphenylphosphine-o-benzylphenylimine (65) :

The irradiation of triphenylphosphine-o-benzylphenylimine (65) in dry benzene in an inert atomsphere of nitrogen gas two products were isolated.



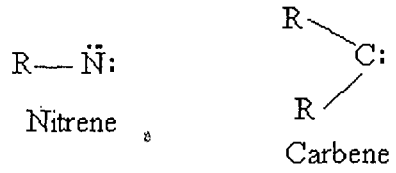
Scheme (7) : Showing the expected photochemical reaction of tripheny phosphine-o-benzyphenylimine

The photochemical products isolated were only the above mentioned, triphylphsophine and o-azobenzylbenzene (65b). However this was probably

due to compling of nitrene type of intermediate. This intermediate did not insert to give the expected product (65a). This could well be a matter of multiplicity of the nitrene.

The P-N Bond Cleavage In Triphenylphosphine-o-benzylphen--ylimine :

From the products which were isolated a nitrene intermediate was proposed.



A nitrene is a species with an electron difficient nitrogen atom. It is analogous to carbene. Similar to carbene, it has two non-bonding electrons which may have antiparallel spins "singlet state" or parallel spins "triplet state".

It is established that nitrene are generated by photolysis or pyrolysis of certain compounds. Its nucleophilicity could be recognized by the type of reaction it undergoes. Singlet electron spin state adds to a double bond "electrophilic singlet" where as triplet state abstracts aliphatic hydrogen atoms "biradical triplet".

The C-N Bond Cleavage In Triphenylphosphine-o-benzyl-phenylimine :

H-Zimmer and M. Jayawant[121] observed the cleavage of C-N bond upon irradiation of triphenylphosphine-t-butylimine in cyclohexene. They postulated that a t-butyl radical formed as a result of C-N cleavage which in turn formed a number of products by reacting with some radicals present in the system.

This finding may be attributed to the fact that the only difference between the two systems, The triphenylphosphine-o-benzylphenylimine in one hand, is found in the substituents on nitrogen atom. In the former is the t-butyl which is aliphatic group, in the latter it is the benzylphenyl which is aromatic group.

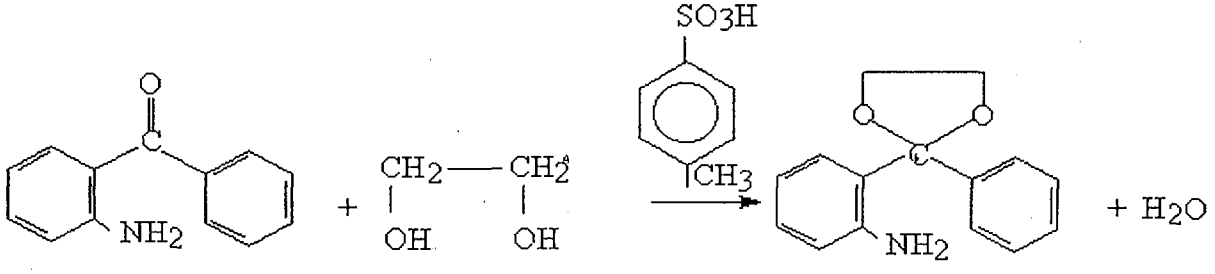
Thus the carbonyl group can stabilize and also strengthen the C-N bond by providing it with certain double bond character brought about by the pair of electrons utilizing the dπ - pπ orbitals of the adjacent P-N bond.

Tscheche[99] however, did not report any observation of C-N bond cleavage upon irradiation of tripheynlphosphinediphenylmethylene [$(C_6H_5)_3P = C(C_6H_5)_2$] in cyclohexene but as mentioned before, all prdoucts he detected originated through cleavage of P=C bond. Consequently in the light of this explanation it does not seen to be surprising that we did not observed C-N bond cleavage upon irradiation of triphenylphosphine-o-benzylphenylimine.

3.4 Reaction of Triphenylphosphine-o-benzophenonimine ethylene acetal (68) :

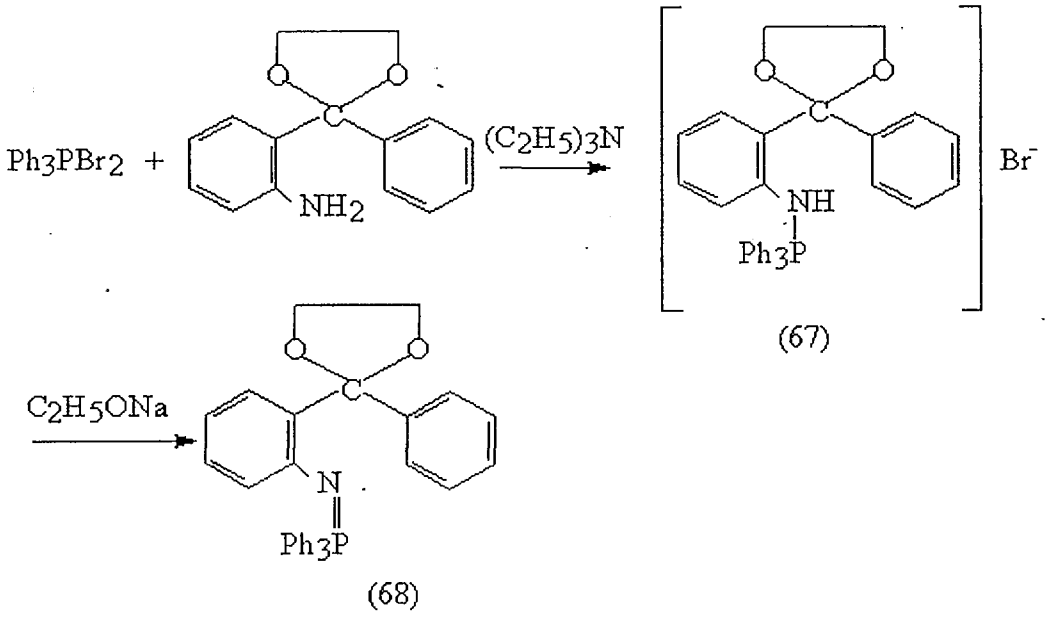
Triphenylphosphine-o-benzophenonimine ethylene acetal (68) was prepared by reacting o-aminobenzophenone, ethylene glycol and p-toluene sulphonic acid. During the reaction the water produced was continuesly removed. o-Aminobenzophenone ethylene acetal (66) was given in good yield.

Triphenylphosphonium-o-benzophenone ethylene acetal bromide (67) was prepared from triphenylphosphonium dibromide and the acetal (66) in presence of triethylamine in an inert nitrogen atomsphere. The phosphonium salt produced was reacted with sodium ethoxide and thus triphenylphosphine-o-benzophenonimine ethylene acetal (68) was given.



(66)

$Ph_3P + Br_2 \longrightarrow Ph_3PBr_2$

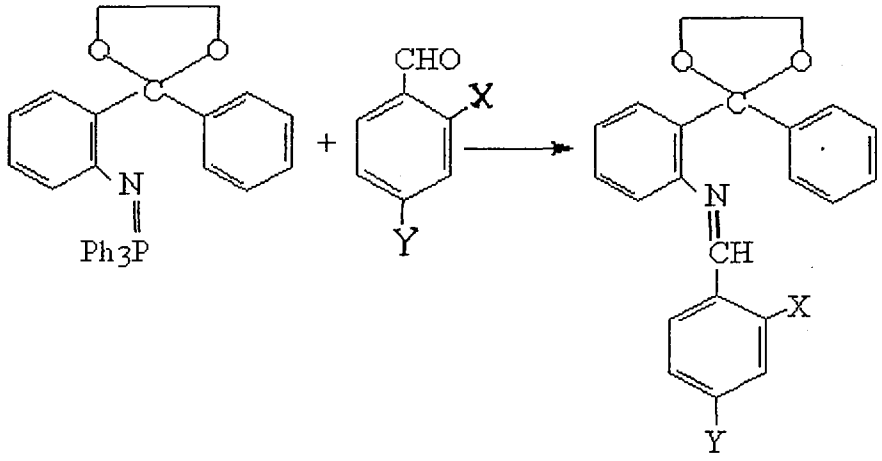


Scheme (8) : Route employed for preparation of triphenylphosphine-o-benzophenonimine ethylene acetal

This different route for the preparation of triphenylphospine-o-benzophenonimine ethylene acetal (68) employed rather than through diazotization of the amine to get to the azide, becuase the sensitivity of acetal to the presence of acids where they get hydrolysed to the starting material. Therefore; to avoid the presence of acid in the diazotization step, nucleophilic displacement of the amino group to one bromide ion on the phosphonium dibromide was used.

This particular compound (68) was prepared to prevent (inhibit) the extensive conjugation which we anticipated to be the reason for the lack of reactivity of triphenylphosphine-o-benzophenonimine. Thus the carbonyl group is transformed to cyclic acetal which no longer takes part in resonance.

Triphenylphosphine-o-benzophenonimine ethylene acetal (68) was separately reacted with benzaldehyde, p-nitrobenzaldehyde and 2,4-dinitrobenzaldehyde, all gave the corresponding schiff's bases



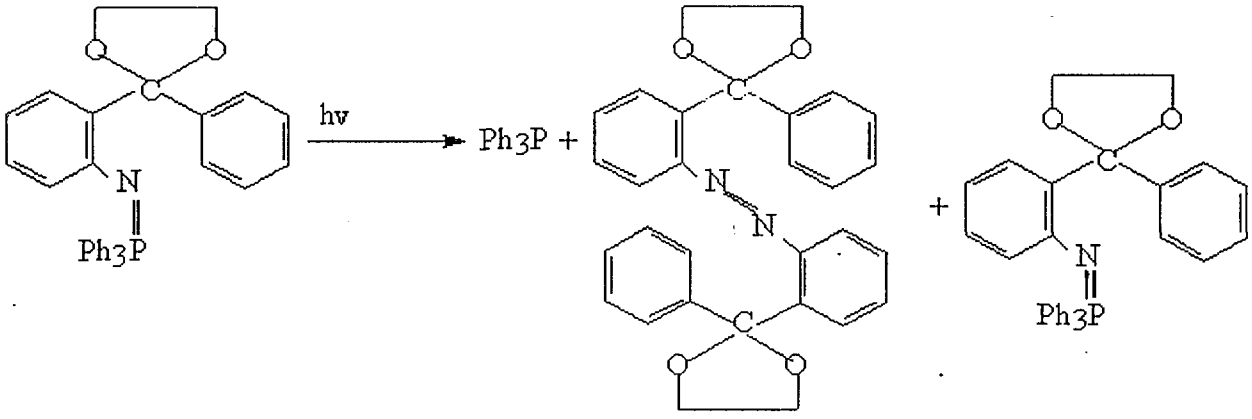
(68a) X = H, Y = H
(68b) X = H, Y = No_2
(68c) X = No_2 Y, No_2

Scheme (9) Reaction of Triphenylphosphine-o-benzophenonimine ethylene acetal with benzaldehyde and it's nitro-substituents.

Now it is seen that absence of carbonyl group from triphenylphosphin-o-benzophenonimine ethylene acetal (68) which is substituted by cyclic ketal did increase its nucleophilicity and became reactive enough to react with different benzaldehydes.

3.4.1 The Photohysis of Triphenylphosphine-o-benzophenonimine ethylene acetal (68) :

Triphenylphosphine-o-benzophenonimine ethylene acetal (68) was irradiated for 10 hours using Hanovia medium pressure UV lamp, three products were isolated and identified as triphenylphosphine, o-azobenzophenone ethylene acetal and starting material



o.Azobenzophenoneethylene acetal

This is also a proof that extensive conjugation in presence of carbonyl group was the reason of unreactivity. [8]

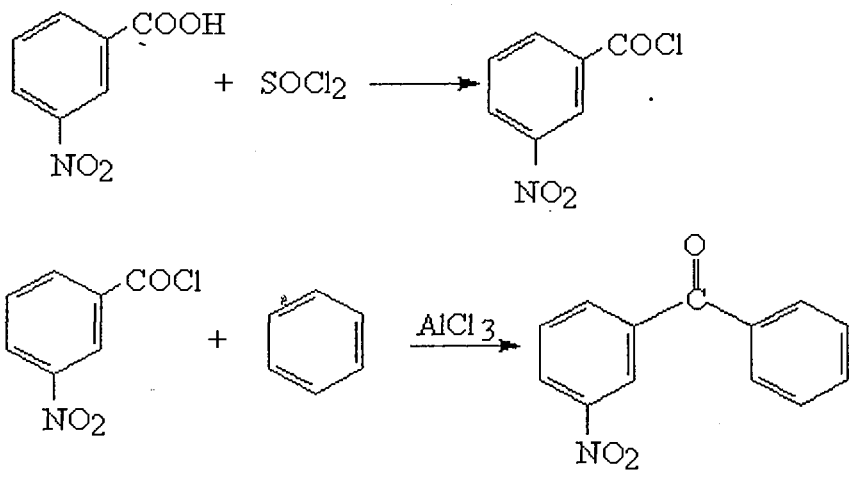
3.5 Attempted Synthesis Of m-Nitrobenzophenone (69):

3.5.1 Nitration Of Benzophenone:

Benzophenone was dissolved in concentrated sulphurie acid at 0°C, then nitrating mixture was introduced dropwise after it was cooled below 5°C. According to the fact that the carbonyl is a meta directing group, we except that the nitration occurs at the meta position, unfortunately upon monitoring by TLC many products were obtained, and this procedure was a bandoned.

3.5.2 Friedle Craft Acylation :

m-Nitrobenzophenone was prepared by treating m-nitrobenzoic acid with thionyl chloride under anhydrous conditions and the excess of thionyl chloride distilled off. Pure m-nitrobenzoyl chloride was reacted with dry benzene in presence of anhydrous aliminium chloride, giving the m-nitrobenzophenone in good yiled

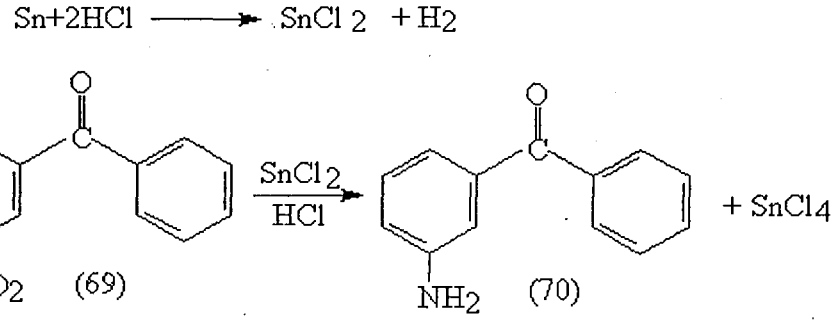


Scheme (10) Preparation of m-nitrobenzohphenone by Friedle Craft acylation.

3.6 Attempted synthesis of m-Aminobenzophenone (70):

3.6.1 Reduction of m-Nitrobenzophenone by Stanous Chloride:

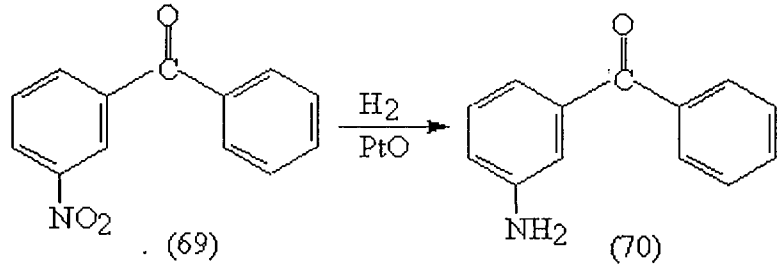
Granulated tin was added to m-nitrobenzophenone and concentrated hydrochloric acid which was added in three equal portions making continous source of hydrogen gas during all reaction period. The resulting amine was in poor yield with great amount of inorganic salt.



Scheme (11) : Preparation of m-Aminobenzophenone by reduction of m-nitrobenzophenone with Stanous Chloride.

3.6.2 Reduction Of m-Nitrobenzophenone By Catalytic Hydrogenation :

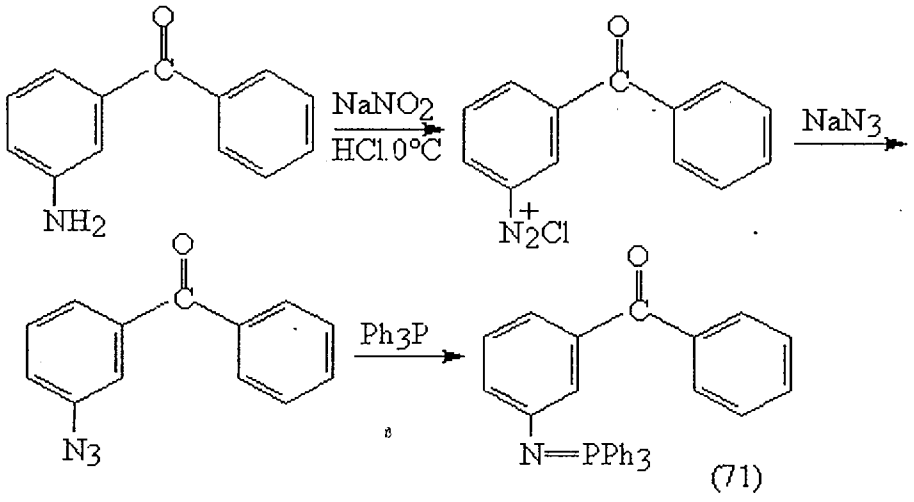
m-Aminobenzophenone was prepared by reduction of m-nitrobenzophenone by hydrogen gas in presence of adam's catalyst (platinum oxide). The percentage yield was very high.



Scheme (12) : Reductionof m-Nitrobenzophenone with hydrogen gas

3.7 Reaction Of Triphenylphosphine-m-Benzophenonimine (71) :

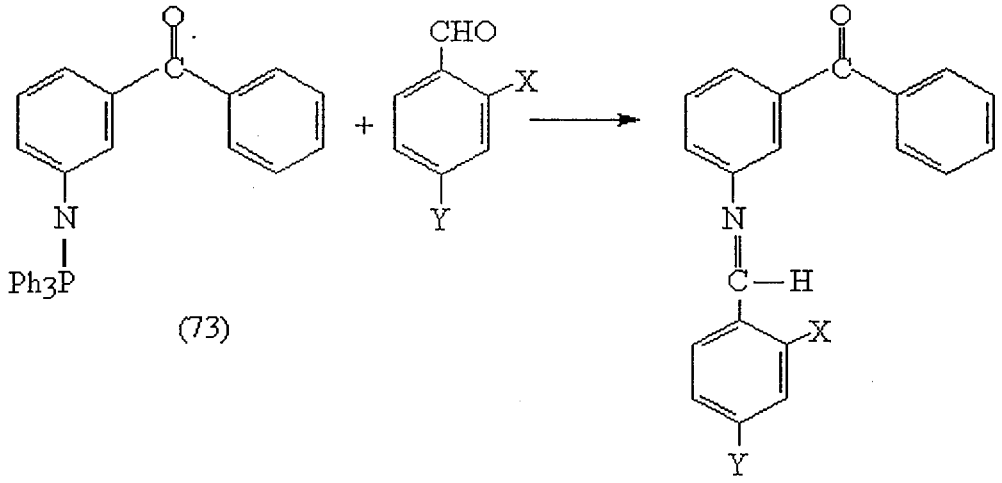
Triphenylphosphine-m-benzophenonimine (71) was prepared by diazotization of m-aminobenzophenone, then treated with a solution of sodium azide. The azide formed dissolved in benzene, then reacted with a solution of triphenylphospohine in benzene to give the desired product in good yield.



Scheme (13) : Route employed for the preparation of triphenylposphine-m-benzophenonimine

Triphenylphosphine-m-benzophenonimine was reacted separately with benzaldehyde, p-nitrobenzaldehyde and 2,4-dinitribenzaldehyde. With benzal-

dehyde it failed to react, however; it did with p-nitrobenzaldehyde and also with 2,4-dinitro-benzaldehyde giving the corresponding schiff's bases



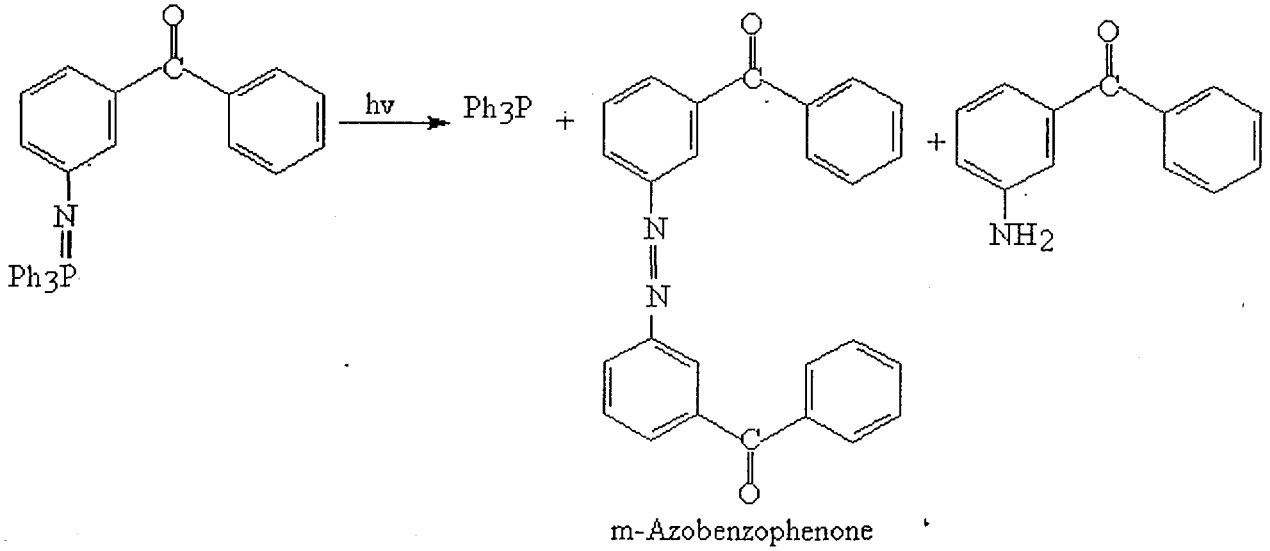
(73a) X = H, Y = No_2

(73b) X = No2, Y = No_2

Scheme (14) reaction of triphenylphospine-m-benzophenominine with p-nitrobenzaldehyde and 2,4-dinitrobenzaldehyde.

3.7.1. The photolysis of Triphenylphosphine-m-benzophenonimine (71):-

Triphenylphosphine-m-benzophenonimine (71) was irradiated for 6 hours using Hanovia medium pressure UV lamp three products were isolated :



It is planned to prepare triphenylposphine-m-benzophenonimine (71) to avoid direct conjugation of electrons on nitrogen with carbonyl group of the

phenone. This also inhibits extensive resonance experienced by the ortho isomer. In so doing nucleophilicity will increase to the extent that it can attack other electrophilies such as the benzaldehydes mentioned above.

This is considered as a third proof that we are right to explain the unreactivity of ortho derivative to exessive conjugation.

CHAPTER FOUR

4. CONCLUSION

One could conclude that, reaction of phosphinimines with the different substituted carbonyl compounds depend mainly on the nucleophilicity of the phosphinimines and the electrophilicity of the carbonyl compound. If both are strong the reaction will be favourable and faster. On the other hand, if both are weak the reaction might not take place.

This clear in the ortho and para derivatives of triphenylphosphine-benzophenonimine which they fail to react chemically and photochemically due to their unreactivity caused by the excessive resonance. It is also observed in the reactivity of the meta, reduced form and the cyclic ketal derivatives, in which the nitrogen is a good nucleophile and the phosphorous-nitrogen double bond is easily cleaved due to the weak overlap between $d\pi$ and $p\pi$ orbitals. This facilitates the Witting type of reaction to give the mentioned products..

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