A Study of the Reactions of Phosphetanium and Vinylphosphonium Salts

by

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in the Faculty of Science

of the

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STATEMENT.

The experimental work described in this thesis has been carried out by the author in the laboratories of the Department of Chemistry of the University of Leicester between October 1966 and May 1969.

No part of this work has been presented or is concurrently being presented for any other degree.

Signed

J.R. Shutt

September, 1969.

J.R. Shutt.

ACKNOWLEDGEMENTS.

The author wishes to record his sincere thanks to Dr. S. Trippett for his supervision, encouragement and inspiration.

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SUMMARY.

Successful and unsuccessful attempts were made to synthesise vinylphosphonium salts containing an active methylene group attached to the phosphorus atom. An investigation was carried out into the use of benzyldiphenylvinylphosphonium bromide in a Wittig reaction without the use of base, by the addition of a nucleophile to the vinyl group followed by proton transfer to give the benzylidene ylid.

The hydrolyses of vinyl- and β-substituted ethyl phosphonium salts were investigated; also the reactions of alkylidenediphenylvinylphosphoranes were studied in an attempt to prepare four membered heterocycles. In both cases, interesting and surprising results were obtained.

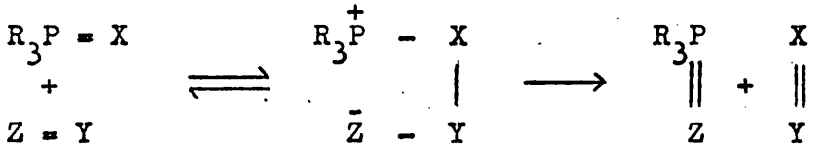
A study was made of the stereochemistry of substitution reactions at the phosphorus atom of phosphetanes. Alkaline hydrolyses of benzyl salts proceed with loss of the benzyl group. One geometrical isomer of 1-benzyl-2,2,3-trimethyl-1-phenylphosphetanium bromide and the corresponding pentamethyl salt hydrolysed with retention of configuration at the phosphorus atom, whereas the other geometrical isomer of these salts hydrolysed with partial inversion of configuration. In comparison, 1-benzyl-2,2,3,3-tetramethyl-1-phenylphosphetanium iodide, possessing no geometrical isomerism, was shown to hydrolyse with complete retention of configuration by optically active techniques. A discussion of the possible mechanisms is presented, ylid inversion being favoured.

Other substitution reactions in phosphetanes brought about either ring expansion or ring opening reactions. All the reactions of phosphetanes were governed by the preference of the four membered ring to occupy an apical-equatorial position in the trigonal-bipyramidal intermediate. Further proof of this preference was obtained by the enhanced stability observed in the pentacoordinate phosphoranes prepared from phosphetanes as compared with the adducts of their acyclic analogues.

INDEX.

The Wittig Reaction.

Wittig and Schöllkopf found[1] that an alkylidenephosphorane reacted with a carbonyl compound forming an intermediate betaine, from which a phosphine oxide was eliminated to give an olefin in which the position of the double bond was not in doubt. This reaction has since been shown to be an example of a more general four-centre rearrangement first noted by Staudinger[2],



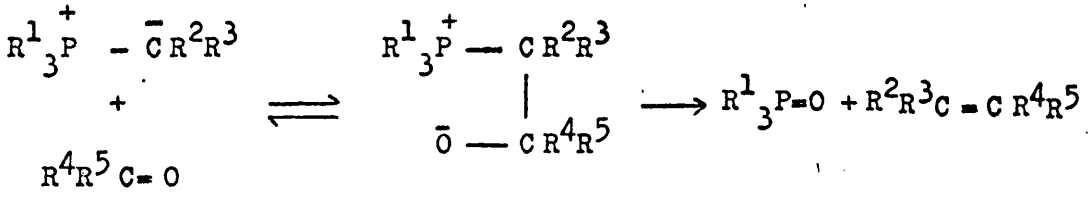
where X and Y can be carbon and/or nitrogen, and where Z, though usually oxygen, may be sulphur, chlorine[3] or the group – NHR[3].

Preparation of Alkylidenephosphoranes.

The alkylidenephosphorane is generated by the action of a suitable base upon the corresponding phosphonium salt. The strength of base required is dependent upon the acidity of the α-hydrogen to be removed, thus the less acidic the α-hydrogen, the stronger the base required.

Mechanism of the Wittig Reaction.

This reaction is a two-stage process involving the reversible addition[4] of an alkylidenephosphorane to a carbonyl compound to give an intermediate betaine (I), from which a phosphine oxide is eliminated to give an olefin.



(I)

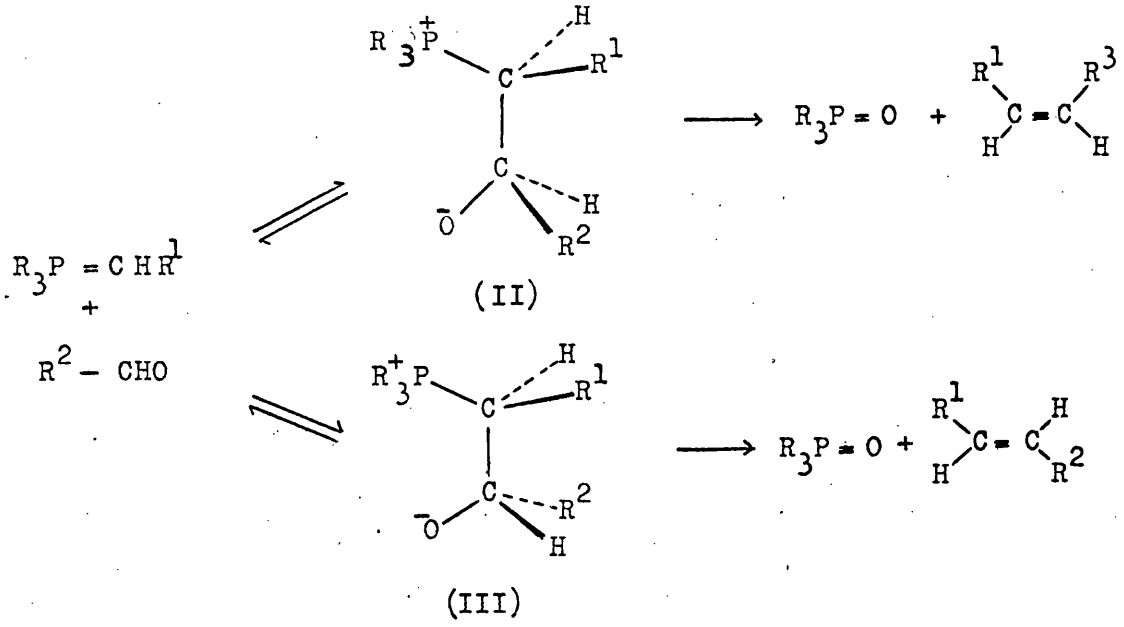
Either of the stages may be rate determining.

The formation of betaine (I) is presumably by the nucleophilic

attack of the α-carbon of the phosphorane on the carbon of the carbonyl group. Consequently the rate of betaine formation is dependent upon the nucleophilicity of the phosphorane and to the susceptibility to nucleophilic attack of the carbonyl group. However, the decomposition of the betaine is hindered by the very groups that aid its formation and vice versa. Electron donating groups at R^1 decrease the positive character of the phosphorus so increasing the nucleophilicity of the phosphorane, whereas the rate of decomposition of the betaine is decreased. Conversely, groups at R^2, R^3, R^4 and R^5 capable of conjugating with the incipient double bond in the transition state so aiding betaine decomposition, hinder betaine formation. Consequently the very nature of the reactants prescribes which step is rate determining.

Stereochemistry of the Resulting Olefin.

Two diastereoisomeric betaines (II) and (III) can be formed in the reaction of a phosphorane with an aldehyde.



(II)

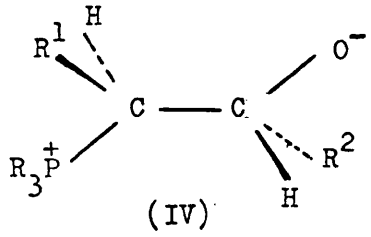
(III)

The betaines (II) and (III) are interconvertible via dissociation to reactants. Dissociation is aided by an activating group at R^1 and hindered by the lack of such a group. Betaine interconversion becomes an important factor when (a) the rate of betaine decomposition is slower than its formation, (b) the starting phosphorane is

relatively stable and (c) the rates of formation of the two olefins are substantially different. When these factors are in operation, one olefin (usually trans) will be formed in preference to the other.

The cis:trans ratio of the resulting olefin from a stabilised phosphorane is thermodynamically controlled. In non-polar solvents and in the absence of added salts, the betaine (III) would be preferred as the electrostatic attraction between the positive and negative centres would hold the betaine in the configuration shown in (III) with the groups R^1 and R^2 not eclipsed. Consequently the trans olefin would predominate in this case [5, 6].

However, in a polar solvent, or in the presence of added salts [7], the electrostatic interaction between $\overset{+}{P}$ and $\overset{-}{O}$ would be greatly reduced so the most stable betaine would be as shown in (IV) with R^1 and R^2 lying trans diaxial. Consequently cis olefin would be preferred.



(IV)

When a non-stabilised phosphorane is used, the interconversion between betaines is greatly reduced. In this situation the stereochemistry of the resulting olefin becomes more kinetically controlled [6, 7].

Stereochemistry at Phosphorus.

By the use of optically active phosphonium salts, it has been found [8] that the Wittig reaction proceeds with retention of configuration at the phosphorus atom.

For more detailed information on the Wittig reaction, the reviews of Hudson [9], Johnson [10], Kirby and Warren [11], Maercker [12], Trippett [13] and Wittig [14] should be consulted.

Vinylphosphonium Salts.

The preparations and properties of vinylphosphonium salts reviewed here are for compounds having four phosphorus-carbon bonds and with one carbon-carbon double bond α,β to the phosphorus atom. Although the first compound of this type was reported in 1861 by A.W. Hofmann[15], interest in this class of compounds was not aroused until a century later.

Preparation of Vinylphosphonium Salts.

1) By Elimination.

Vinylphosphonium salts have been prepared from β-substituted ethylphosphonium salts, where the β-substituent X was a reasonably good leaving group. This elimination was usually, though not always, base catalysed. Where base catalysis was required, the initial step was presumably the removal of an α-proton to give an ylid, followed by loss of the β-substituent X.

$$R_3\overset{+}{P}CH_2CH_2X\ \ Y^- \longrightarrow R_3\overset{+}{P}\overset{-}{C}H\ CH_2X \longrightarrow R_3\overset{+}{P}CH{:}CH_2\ \ Y^-$$

(V)

Grayson[16,17] prepared a series of β-acetoxyethylphosphonium salts (V : R = alkyl, cyclohexyl, aryl; X = OAc), which on treatment with sodium carbonate solution formed vinylphosphonium salts by the elimination of acetic acid.

Treatment of (V ; R = Ph, X = Br) with moist silver oxide[18], also gave the vinyl salt. The same workers also used phenyllithium as the base, but in this case the vinyl salt was used *in situ*[18]. Another *in situ* preparation[18,19] was the treatment of ethylenebis(triphenylphosphonium) dibromide (VI) with one equivalent of phenyllithium. In this case elimination of triphenylphosphine from the ylid intermediate occurred.

$$Ph_3\overset{+}{P}CH_2CH_2\overset{+}{P}Ph_3 \quad (VI) \quad 2\,Br^- \xrightarrow{PhLi} Ph_3\overset{+}{P}\overset{-}{C}H\,CH_2\overset{+}{P}Ph_3 \quad Br^- \longrightarrow Ph_3\overset{+}{P}CH{:}CH_2\;Br^- + Ph_3P$$

Eliminations in acid conditions have also been reported[20]. Treatment of 1-hydroxy-2-methylpropyltriphenylphosphonium bromide (VII) with refluxing 48% HBr solution gave 1-methylvinyltriphenylphosphonium bromide (VIII).

$$(CH_3)_2\underset{OH}{\underset{|}{C}}-\overset{+}{P}Ph_3\;\;Br^- \xrightarrow{48\%\ HBr} CH_2{:}\underset{CH_3}{\underset{/}{C}}-\overset{+}{P}Ph_3\;\;Br^-$$

(VII) (VIII)

Schweizer and Bach reported that base was not required for the elimination of phenol from 2-phenoxyethyltriphenylphosphonium bromide. This salt was stirred in refluxing ethyl acetate for three days, after which time elimination of phenol had been accomplished.

2. Quaternisations with Vinylic Systems.

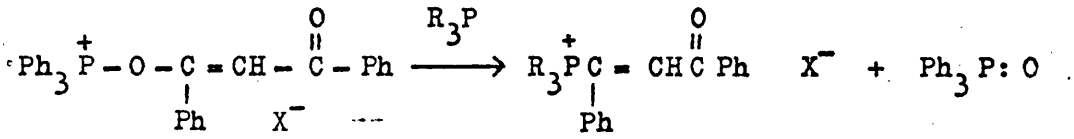
Quaternisation of a tertiary phosphine with a vinyl halide does not occur under ordinary conditions. However, if activated vinyl halides are used quaternisation proceeds quite readily. This was first noted by Zbiral[21], who quaternised triphenylphosphine with a series of acylvinyl halides (IX: $R^1 = CH_3$, Et, Pr, Ph)

$$R_3P + XCH{:}CH-\overset{O}{\overset{\|}{C}}R^1 \longrightarrow R_3\overset{+}{P}CH{:}CH\overset{O}{\overset{\|}{C}}R^1\;X^-$$

(IX) (X)

Further work on this reaction was carried out by Walker[22], who found that both cis and trans olefins gave only the trans double bond in the vinyl salt (X; R = Bu, Ph; X = Cl, Br; R^1 = COOMe, CN).

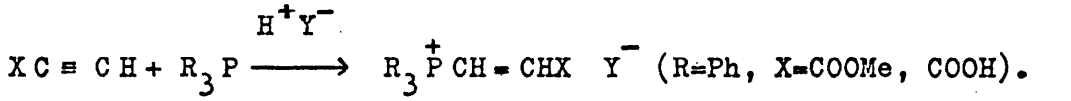
Treatment of the quasi-phosphonium salt (XI) with a more nucleophilic phosphine or with excess triphenylphosphine gave the substituted vinylphosphonium salt[23]. No reaction conditions or yield were given for this reaction.



(XI)

Quaternisation of a tertiary phosphine with an unreactive halide such as bromobenzene can be accomplished by the use of a nickel or cobalt salt[24]. In this way, Gallagher[25] was able to quaternise β-styryl bromide with triphenylphosphine to give triphenylstyrylphosphonium bromide.

If an acetylene is activated by an electron withdrawing group, then in strong acid solution, tertiary phosphines were found to add to the triple bond to give substituted vinylphosphonium salts (XII)[26].



(XII)

3. Quaternisations of Vinylphosphines.

Although there are several reports of the preparation of vinylphosphines, only in a few cases has quaternisation been carried out.

Savage and Trippett[27] prepared diphenyl-1-phenylvinylphosphine by the nucleophilic attack of sodium diphenylphosphide on α-bromostyrene. The resulting phosphine was then quaternised with methyl iodide or benzyl bromide to give the corresponding phosphonium salt.

Aguiar[28] has prepared a number of phenyl substituted vinylphosphines in a similar manner and also by the action of lithium diphenylphosphide on an acetylene[29]. The stereochemistry of the resulting vinylphosphine was governed by the presence or absence of certain primary, secondary and tertiary amines.

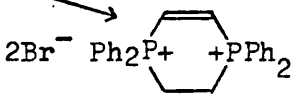
$Ph_2PLi + HC \equiv C\,Ph \xrightarrow{T.H.F.} Ph_2PCH \overset{t}{=} CHPh$

(XIII)

$\xrightarrow[Bu_2NH]{T.H.F.} Ph_2PCH \overset{c}{=} CHPh$

$ClHC = CHCl + 2LiPPh_2 \xrightarrow{T.H.F.} Ph_2PCH = CHPPh_2 \xrightarrow{BrCH_2CH_2Br}$

(XIV)



The diphosphine (XIV) was quaternised[30] with ethylene dibromide to give the 1,4-diphosphacyclohexene (XV) and diphenylstyrylphosphine (XIII) was quaternised[25] by the complex salt method[26] to give triphenylstyrylphosphonium bromide.

4. Involving Isomerisations and Phosphoranes.

The isomerisation of readily accessible allylphosphonium salts (XVI) to propenyl salts (XVII) can be accomplished[17] by the use of benzyltrimethylammonium hydroxide in acetonitrile.

$R_3\overset{+}{P}CH_2CH = CH_2\ X^- \longrightarrow R_3\overset{+}{P}CH = CHCH_3\ X^-$

(XVI) (XVII)

Allylphosphonium salts have also been used[31] for the preparation of γ-acylpropenyl salts. The allyl salt with phenyllithium gave an allylidenephosphorane, which on treatment with an acyl chloride gave an γ-acylpropenyl salt (XVIII).

$Ph_3\overset{+}{P}CH_2CH{:}CH_2\ Br^- \xrightarrow{PhLi} Ph_3\overset{+}{P}-\overset{-}{C}H-CH{:}CH_2 \xrightarrow{R-\overset{O}{\overset{\|}{C}}-Cl} Ph_3\overset{+}{P}-CH{:}CHCH_2\overset{O}{\overset{\|}{C}}R\ Cl^-$

(XVIII)

It has also been reported[32] that bromotriarylphosphonium bromides reacted with N-propenylpiperidine to give N-piperidino substituted vinylphosphonium salts.

$Ar_2PBr_2 + CH_3.CH{:}CH.N\langle\rangle \longrightarrow Ar_3\overset{+}{P}-\underset{CH_3}{\underset{|}{C}}{:}CH.N\langle\rangle\ Br^-$

Vinylphosphonium salts have also been prepared by the addition of hydrogen halides to vinylidenephosphoranes. Addition of hydrogen bromide to the complex produced by the action of triphenylphosphine on 2,2-diphenylvinylmagnesium bromide gave 2,2-diphenylvinyltriphenylphosphonium bromide (XIX) [33].

$$Ph_3P + Ph_2C{:}CH\,MgBr \xrightarrow[2)\ HBr]{1)\ O_2} Ph_3\overset{+}{P}.CH{:}CPh_2\ Br^-$$

(XIX)

Another 2,2-disubstituted vinylphosphonium salt (XX) was obtained by the addition of hydrogen chloride to the phosphorane (XXI), from the reaction of hexafluoroacetone with hexaphenylcarbodiphosphorane[34].

$$Ph_3P{:}C{:}PPh_3 + (CF_3)_2C{+}O \longrightarrow Ph_3P\underset{O-C(CF_3)_2}{\overset{|}{-}}C = PPh_3 \longrightarrow \begin{matrix} Ph_3P = O \\ + Ph_3P{:}C{:}C(CF_3)_2 \\ \text{(XXI)} \end{matrix}$$

$$\xrightarrow{HCl} Ph_3\overset{+}{P} - CH{:}C(CF_3)_2\ Cl^-$$

(XX)

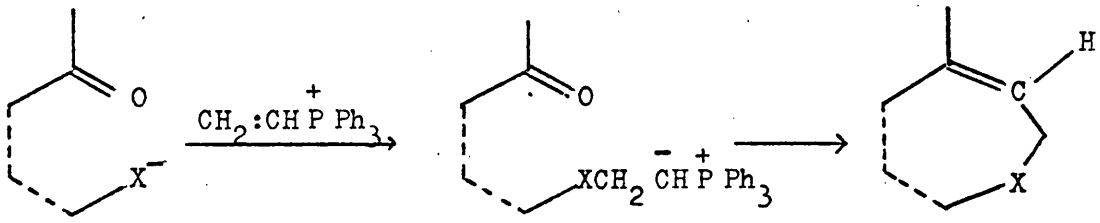
Properties of Vinylphosphonium Salts.

The presence of a positively charged phosphorus atom adjacent to the double bond means that the β-carbon atom of the vinyl group is very susceptible to nucleophilic attack. A study[35] of the kinetics of the addition of alcohols to the double bond of vinylic compounds has shown that for the addition of methanol, the rate was greatest when $X = -\overset{+}{P}R_3$ and that the rate determining step was the attack of the nucleophile on the β-carbon atom.

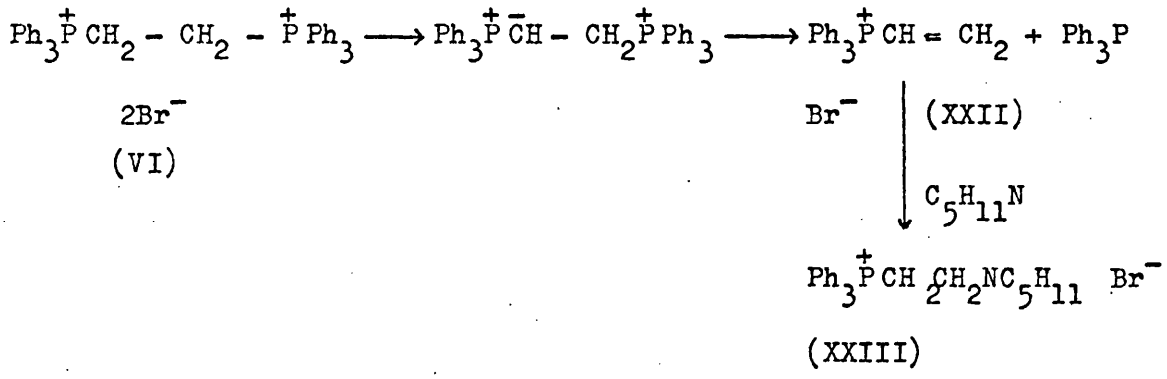
$$CH_2{:}CHX + ROH \rightleftharpoons R-\overset{+}{\underset{H}{O}}-CH_2-\bar{C}HX \longrightarrow RO\,CH_2\,CH_2\,X$$

where $X = -\overset{O}{\overset{\|}{C}}NHR$, $-\overset{O}{\overset{\|}{C}}R$, SO_2NR_2, $-CN$, SO_2R, $-\overset{O}{\overset{\|}{C}}R$ and $-\overset{+}{P}R_3$

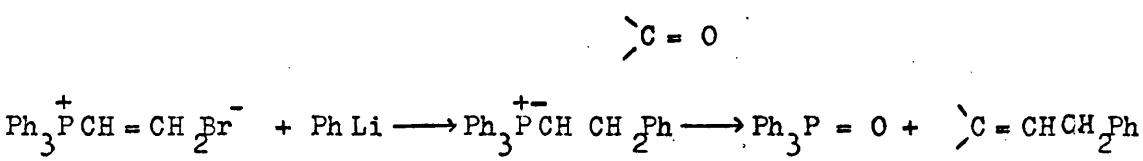
This susceptibility to nucleophilic attack has been reported for several nucleophiles[17,20]; such as >N-H, S-H, O-H and their respective anions, $R_3P \cdot HBr$ and active methylene groups. This property has been used very successfully by Schweizer in an elegant ring synthesis [36,37,38,39] and in a chain lengthening reaction[40].



Organolithium reagents, phenyl-[18] and N-piperidyl-[19], but not n-butyl-[27], have been found to add to the vinyl group. Wittig[19] used this property to show that the intermediate in the decomposition of ethylene-bis-(triphenylphosphonium) dibromide (VI) by an organolithium reagent, was triphenylvinyl-phosphonium bromide (XXII), which he isolated as the β-N-piperidinoethyl salt (XXIII).



Phenyllithium also added to the vinyl group[18] to give a phosphorane (XXIV), which could then undergo the Wittig olefin synthesis.

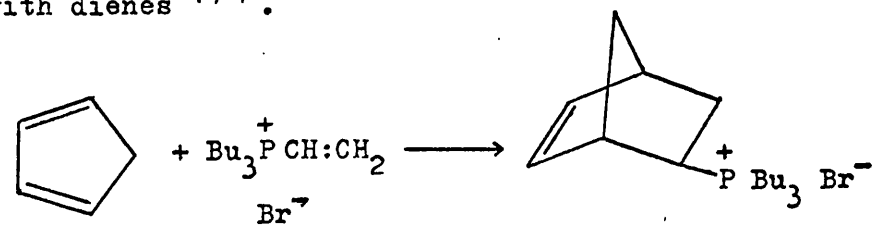


(XXXIV)

However, when substituted vinylphosphonium salts are used, where substitution was on the β -carbon atom of the vinyl group, these additions to the double bond occurred less readily or did not occur at all[17]. For example, treatment of triphenylpropenylphosphonium bromide with phenyllithium gave only 6% of the phosphorane by addition to the vinyl group. Further, it was found[33] that treatment of 2,2-diphenylvinyltriphenylphosphonium bromide (XIX) with phenyllithium gave only the vinylidenephosphorane (XXV) and no addition product.

$$\underset{\text{(XIX)}}{Ph_3\overset{+}{P}-CH=CPh_2\ Br^-} \xrightarrow{PhLi} \underset{\text{(XXV)}}{Ph_3P=C=CPh_2} \xrightarrow{Ph_2C=O} Ph_3P=O + Ph_2C=C=CPh_2$$

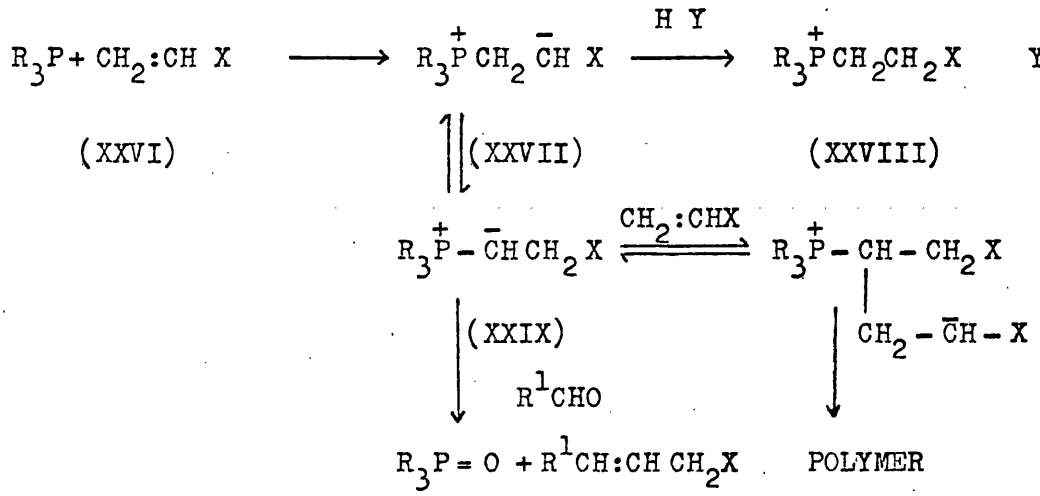
The vinyl group can react as a dienophile to give Diels-Alder adducts with dienes[17,41].



Vinylphosphonium Salt Preparation.

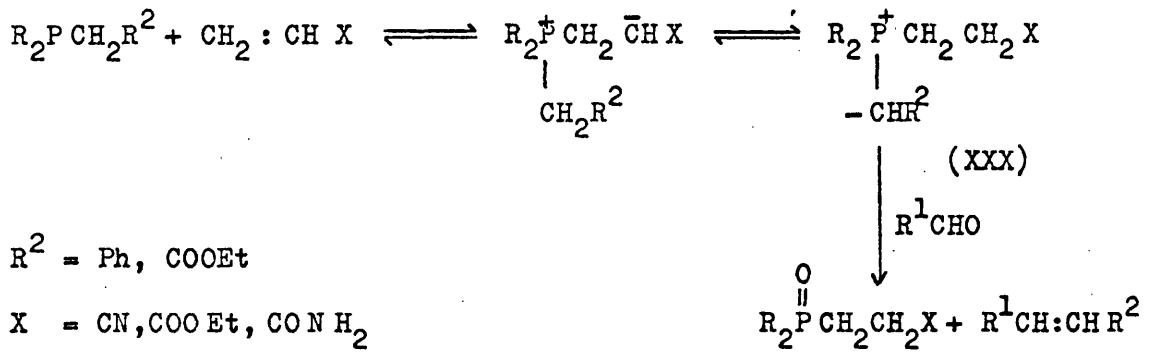
The initial aim of the work described in this section of the thesis was to devise a synthesis of phosphoranes for use in the Wittig reaction without the use of base.

It has been noted by several workers[42-46] that trivalent phosphorus compounds reversibly add to the double bond of an activated olefin (XXVI) to give a betaine (XXVII).



In the presence of acid this betaine (XXVII) was protonated[44] to give the β-substituted ethylphosphonium salt (XXVIII). In the absence of acid, proton transfer occurred to give the relatively more stable alkylidenetriphenylphosphorane (XXIX). This phosphorane might then react with further molecules of the activated olefin[42], or if a carbonyl compound was present, the Wittig reaction would take place[47].

Trippett[48] adapted this last mode of reaction by replacing triphenylphosphine with a phosphine of the type $R_2P\,CH_2R^2$, where R^2 is a group capable of stabilising an adjacent carbanion. This phosphine reacted with activated olefins to give a betaine, in which proton transfer took place giving the ylid (XXX). This ylid subsequently underwent the Wittig reaction.



R^2 = Ph, COOEt

X = CN, COOEt, $CONH_2$

However, the disadvantage of this scheme is that the group R^2CH_2 must be introduced at the phosphine stage and such a phosphine becomes more difficult to handle and the choice of group R^2 slightly restricted. As an alternative approach to this scheme, an attempt was made to synthesise benzylvinylphosphonium salts by the quaternisation of diphenylvinylphosphine, a much more stable compound. These vinylphosphonium salts would then be treated with a powerful nucleophile, but weak base in an attempt to form ylids of type (XXX).

Synthesis of Vinylphosphonium Salts.

1. Quaternisation of Diphenylvinylphosphine.

Quaternisation of diphenylvinylphosphine[49] with reactive alkyl bromides in an aprotic solvent yielded only amorphous materials of apparent molecular weight 1000 to 1250 in ethanol. These compounds were polymeric in structure, had no melting point and gave ^1H N.M.R. spectra with very broad, ill defined peaks. Alkaline hydrolysis of the material obtained from the quaternisation with benzyl bromide gave a glassy, polymeric phosphine oxide with an N.M.R. spectrum resembling that of the parent salt.

However, when quaternisation was carried out with methyl iodide or benzyl iodide, the corresponding monophosphonium salt (XXXI; R = H, Ph. X = I) was produced in high yield.

The mechanism for polymer formation was presumably the successive addition of phosphine to the vinyl group of a phosphonium salt.

$$Ph_2PCH:CH_2 + RCH_2X \xrightarrow{k_1} Ph_2\overset{+}{P}(CH_2R)CH:CH_2 \quad X^-$$

(XXXI)

$$Ph_2\overset{+}{P}(CH_2R)CH:CH_2\ X^- + Ph_2PCH:CH_2 \xrightarrow{k_2} Ph_2\overset{+}{P}(CH_2R)CH(CH_2)\overset{+}{P}Ph_2(CH:CH_2)\ X^-$$

$$\downarrow Ph_2PCH:CH_2$$

polymer

As alkyl iodides are more reactive than their corresponding alkyl bromides, then in the quaternisations with the former (R = H, Ph. X = I), the rate of initial quaternisation (k_1) is greater than the rate of nucleophilic attack of the phosphine on the salt (XXXI) (k_2). Thus all the vinylphosphine will be quaternised before Michael addition to the vinyl group can occur. However, in quaternisation with the latter (R = Ph, $-\overset{O}{\overset{\|}{C}}Ph$, $-CO_2Et$. X = Br), the two rates k_1 and k_2 are either similar or k_1 is less than k_2. In this case subsequent Michael addition would occur as soon as salt (XXXI) was formed, resulting in polymeric material.

In an attempt to reduce the nucleophilicity of the phosphine, the quaternisations with reactive alkyl bromides were repeated, using methanol as solvent[9]. Under these conditions benzyl bromide gave benzyl-2-methoxyethyldiphenylphosphonium bromide (XXXII), whilst allyl bromide gave a bis salt having the formula $C_{32}H_{38}Br_2O_2P_2$. Phenacyl bromide and ethyl bromoacetate once again gave polymeric material.

The quaternisation with benzyl bromide in methanol was repeated in the presence of propionaldehyde in order to trap the possible phosphorane intermediate in the formation of salt (XXXII). Under these conditions a small quantity of the highly insoluble bis-salt (XXXIII) was formed in addition to the monophosphonium salt (XXXII).

$$Ph_2\overset{+}{P}(CH_2Ph)CH_2CH_2OCH_3\ Br^-$$

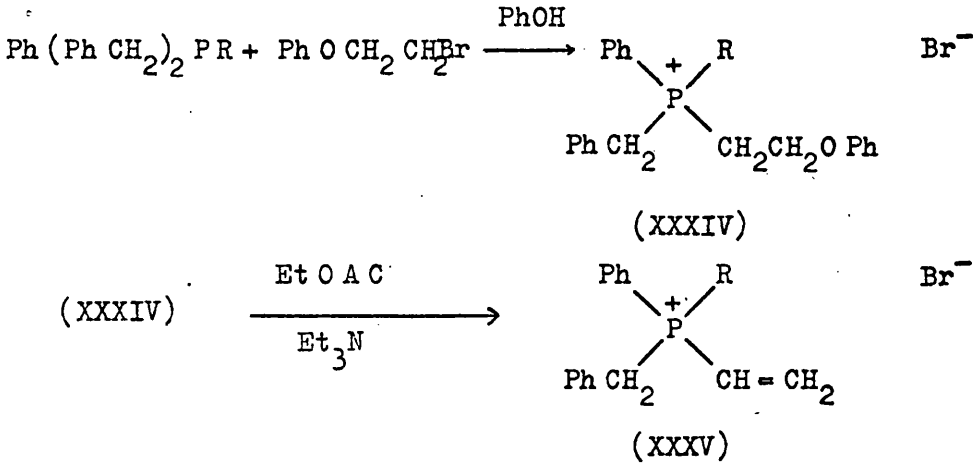
(XXXII)

$$Ph_2\overset{+}{P}(CH_2Ph)CH_2CH_2\overset{+}{P}Ph_2(CH:CH_2)\quad 2\ Br^-$$

(XXXIII)

2. Elimination of phenol.

Benzylvinylphosphonium salts were also prepared by the method of Schweizer[20]. Quaternisation of dibenzylphenylphosphine[50] with β-bromophenetole in phenol gave dibenzyl-2-phenoxyethylphenylphosphonium bromide, (XXXIV: R = CH_2Ph), which on refluxing in ethyl acetate, containing a trace of triethylamine, gave dibenzylphenylvinylphosphonium bromide (XXXV; R = CH_2Ph) in high yield. The required use of base in this elimination reaction is contrary to that reported[20] for 2-phenoxyethyltriphenylphosphonium bromide,



Repeating this reaotion scheme with benzyldiphenylphosphine[51] gave benzyl-2-phenoxyethyldiphenylphosphonium bromide (XXXIV; R= Ph) and benzyldiphenylvinylphosphonium bromide (XXXV; R = Ph).

When an impure sample of dibenzylphenylphosphine was quaternised with β-bromophenetole in phenol, ethylene bis (dibenzylphenylphosphonium) dibromide (XXXVI) was produced. Hydrolysis of this salt with ethanolic sodium hydroxide solution gave two isomeric phosphine oxides (XXXVII) having similar mass spectral properties, but different melting points and solubilities in chloroform. The lower melting phosphine oxide is believed to be a mixture of the d and l forms, whereas the higher melting sample is believed to be the meso form.

$$(PhCH_2)_2\overset{Ph}{\overset{|}{\underset{+}{P}}}CH_2CH_2\overset{Ph}{\overset{|}{\underset{+}{P}}}(CH_2Ph)_2 \quad 2Br^- \xrightarrow{NaOH} PhCH_2\overset{O}{\overset{\|}{\underset{Ph}{\overset{|}{P}}}}CH_2CH_2\overset{O}{\overset{\|}{\underset{Ph}{\overset{|}{P}}}}CH_2Ph$$

(XXXVI) (XXXVII).

3. Quaternisation of 2-phenoxyethyldiphenylphosphine.

2-phenoxyethyldiphenylphosphine (XXXVIII) was prepared by the addition of β-bromophenetole to sodium diphenylphosphide. This phosphine was found to decompose at room temperature[52] such that once decomposition had begun, quaternisation no longer produced the 'normal' monophosphonium salt. Consequently, in the preparation of the phosphine the temperature had to be maintained at or very near 0°C, and once prepared the ethereal solution of the phosphine had to be used immediately. Quaternisation of the freshly prepared phosphine with benzyl bromide was found to be unaffected by the presence of acid, base, radical initiator and inhibitor, and 2-phenoxyethyldiphenylphosphine oxide (XXXIX). In all these cases the 'normal' monophosphonium salt was produced.

Quaternisation of the freshly prepared phosphine with methyl iodide, benzyl bromide, ethyl bromoacetate, allyl bromide and phenacyl bromide gave the corresponding phosphonium salts (XL; (a) R = Ph, (b) R = CO_2Et; (c) R = $CH:CH_2$, (d) R = C(:O)Ph).

$$Ph_2\overset{O}{\overset{\|}{P}}CH_2CH_2OPH \xleftarrow{H_2O_2} Ph_2PCH_2CH_2OPh \xrightarrow{MeI} MePh_2\overset{+}{P}CH_2CH_2OPh \quad I^-$$

(XXXIX) (XXXVIII)

$$\downarrow RCH_2Br$$

$$Ph_2\overset{+}{P}\begin{matrix}CH_2R\\ \diagdown\\ CH_2CH_2OPh\end{matrix}Br^- \xrightarrow[Et_3N]{EtOAC} Ph_2\overset{+}{P}\begin{matrix}CH_2Ph\\ \diagdown\\ CH=CH_2\end{matrix} \quad Br^-$$

(XL) when R = Ph

However, the successful elimination of phenol to give the vinyl salt was only accomplished in the salt (XLa) where R was phenyl. Attempted eliminations from the other salts (XL-b, c, d) yielded oily products

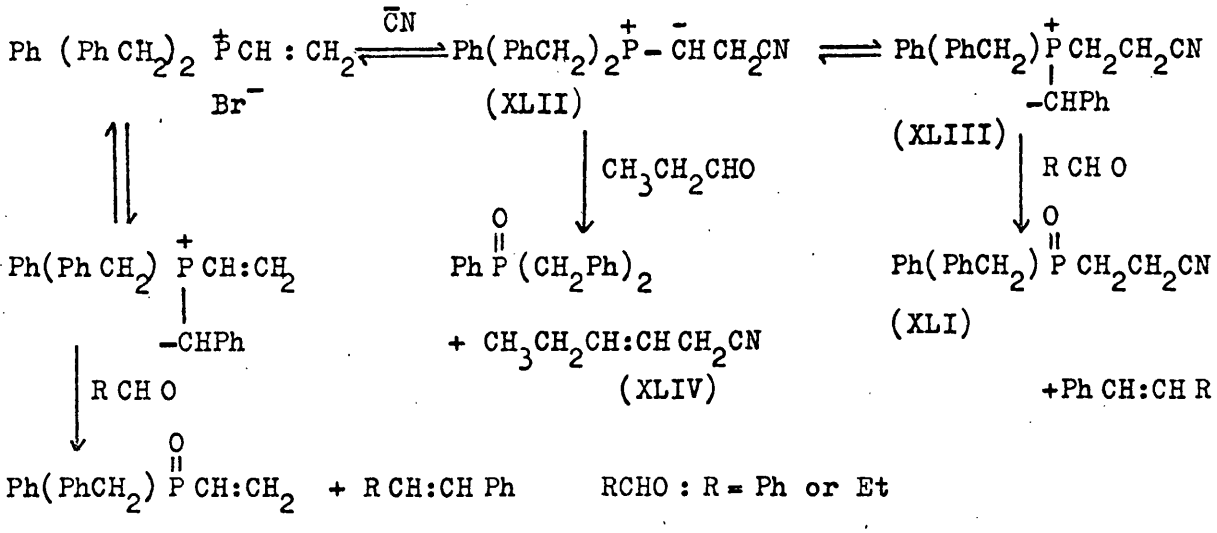
whose spectral properties closely resembled those of the amorphous materials obtained in the quaternisations of diphenylvinylphosphine.

When an 'old' sample of 2-phenoxyethyldiphenylphosphine was quaternised with benzyl bromide, a highly insoluble white solid was produced, whose infrared spectrum indicated a phosphonium salt. Alkaline hydrolysis of this phosphonium salt yielded 1,2-bis(diphenylphosphinyl)-ethane and benzyldiphenylphosphine oxide.

Nucleophilic Attack on the Vinyl Group.

The nucleophilic addition of an anion to the vinyl group of a benzylvinylphosphonium salt was investigated in an attempt to generate a benzylidenephosphorane. The two anions selected for this study were the azide and the cyanide ions as both are powerful nucleophiles yet weak bases. As it was found that these two anions exhibited similar properties in the reactions carried out, the following discussion will only refer to the cyanide anion.

G.L.C. analysis of a methanolic solution of equimolar quantities of potassium cyanide and dibenzylphenylvinylphosphonium bromide with excess benzaldehyde showed the presence of *cis* and *trans* stilbenes (45%). When benzaldehyde was replaced by *p*-chlorobenzaldehyde in this reaction, then *cis* and *trans* 4-chlorostilbene were produced. However, none of the expected benzyl-2-cyanoethylphenylphosphine oxide (XLI) could be detected.



Subsequent experiments showed that the cyanide anion was in fact a sufficiently powerful base to remove a benzylic proton from any benzylphosphonium salt. Further, it was found that the base present in the glass of the reaction flask was sufficient to generate a benzylidenephosphorane, which in the presence of benzaldehyde gave stilbene! The yield and the cis to trans ratio of stilbene varied according to the ratio of surface area of glass to volume of solution, and to the 'history' of the glass vessel. This was found to be applicable to a wide range of benzylphosphonium salts. Certainly, no stilbene was produced when the reaction was carried out in a platinum vessel.

If benzaldehyde was replaced by propionaldehyde (R = Et), then cis and trans β-ethylstyrene and cis and trans hex-3-en-1-nitrile (XLIV) could be detected. The presence of hex-3-en-1-nitrile indicated that addition of the cyanide anion to the vinyl group had occurred to give the β-cyanoethylidenephosphorane (XLII). However, β-ethyl styrene could have been produced either by proton transfer in phosphorane (XLII) to give the benzylidenephosphorane (XLIII), or by direct removal of a benzylic proton from the vinyl salt by the cyanide ion.

A further example of the nucleophilic attack of cyanide ion on the vinyl group of a phosphonium salt was found in the preparation of a sample of hex-3-en-1-nitrile. The ylid (XLV) formed by the attack of cyanide ion on triphenylvinylphosphonium bromide was trapped by propionaldehyde in a Wittig olefin synthesis.

$$Ph_3\overset{+}{P}CH{:}CH_2\ Br^- + KCN \rightleftharpoons \underset{(XLV)}{Ph_3\overset{+}{P}\overset{-}{C}H\,CH_2\,CN} \xrightarrow{CH_3CH_2CHO} Ph_3P{=}O + CH_3CH_2CH{:}CH\,CH_2CN$$

When potassium cyanide was added to a methanolic solution of acrylonitrile and triphenylvinylphosphonium bromide in an attempt to form the dimer of acrylonitrile[42, 46], triphenylphosphine was isolated in good yield as its methiodide. However, no dimer or polymer of acrylo-

nitrile could be detected. When the experiment was repeated in the absence of acrylonitrile, triphenylphosphine was again produced in a similar yield. A solution infrared spectrum indicated the presence of acrylonitrile.

$$Ph_3\overset{+}{P}CH{:}CH_2\ \ Br^- + \overset{-}{C}N \rightleftharpoons Ph_3\overset{+}{P}\overset{-}{C}H\,CH_2CN \rightleftharpoons Ph_3\overset{+}{P}CH_2\overset{-}{C}H\,CN \rightleftharpoons Ph_3P + CH_2{:}\,CH\,CN$$

(XLV) (XLVI).

The mechanism is presumably the initial attack of cyanide ion on the vinyl group of the phosphonium salt to give the phosphorane (XLV). This phosphorane (XLV) would be in equilibrium with phosphorane (XLVI) even though the $-\overset{+}{P}R_3$ group is better able to stabilise an adjacent carbanion than the cyano group. Phosphorane (XLVI) would give triphenylphosphine and acrylonitrile in an equilibrium reaction known to lie predominantly on the side of the phosphine[47].

This reaction is similar to that reported by Horner [53] for allyl-arsonium and -phosphonium salts, where treatment of allyl salt with cyanide ion gave a substituted acrylonitrile and either triphenyl-arsine or -phosphine. A possible explanation for his observations could be the isomerisation of the alkyl group to propenyl followed by the attack of cyanide anion on the β-carbon atom of the propenyl group. The isomerisation process from alkyl to propenyl could be aided by the presence of cyanide ion. The mechanism is visualised as follows:

$$Ph_3\overset{+}{P}CH_2\,CH{:}\,CH_2\ \ Br^- \overset{\overset{-}{C}N}{\rightleftharpoons} Ph_3\overset{+}{P}\overset{-}{C}H\,CH{:}CH_2 \longleftrightarrow Ph_3\overset{+}{P}CH{:}CH\overset{-}{C}H_2$$

$$\Big\downarrow H^+$$

$$Ph_3\overset{+}{P}CH_2\overset{-}{C}(CN)\,CH_3 \rightleftharpoons Ph_3\overset{+}{P}\overset{-}{C}H\,CH(CN)\,CH_3 \overset{\overset{-}{C}N}{\rightleftharpoons} Ph_3\overset{+}{P}CH{:}\,CH-CH_3$$

$$\Big\downarrow$$

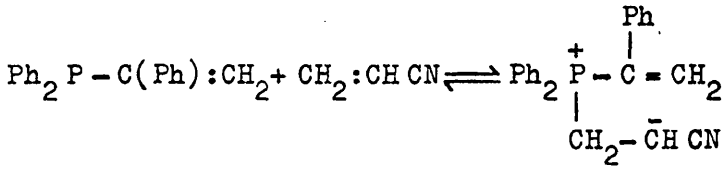
$$Ph_3P + CH_2{:}\,C(CN)\,CH_3$$

Conclusion.

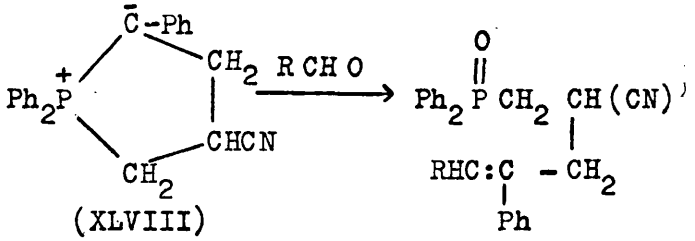
This work showed that nucleophilic anions would add to the β-carbon of a vinylphosphonium salt. However, the olefin formed from the subsequent Wittig reaction was too dependent upon the basicity of the anion and the reactivity of the aldehyde to be of any general use. The difficulty experienced in the synthesis of benzylvinylphosphonium salts and the failure in the synthesis of vinyl salts containing other reactive methylene groups adjacent to the phosphorus atom, denied this process any great flexibility.

Reactions of the Ylids of Vinyl Salts.

As part of an investigation into the susceptibility of 1-phenylvinyl salts to Michael addition, Savage and Trippett[27] found that diphenyl-1-phenylvinylphosphine reacted with acrylonitrile to give a betaine (XLVII), which cyclised by internal Michael addition to give the cyclic ylid (XLVIII) stabilised by the ∝-phenyl group. This ylid reacted with an aldehyde in a Wittig reaction.

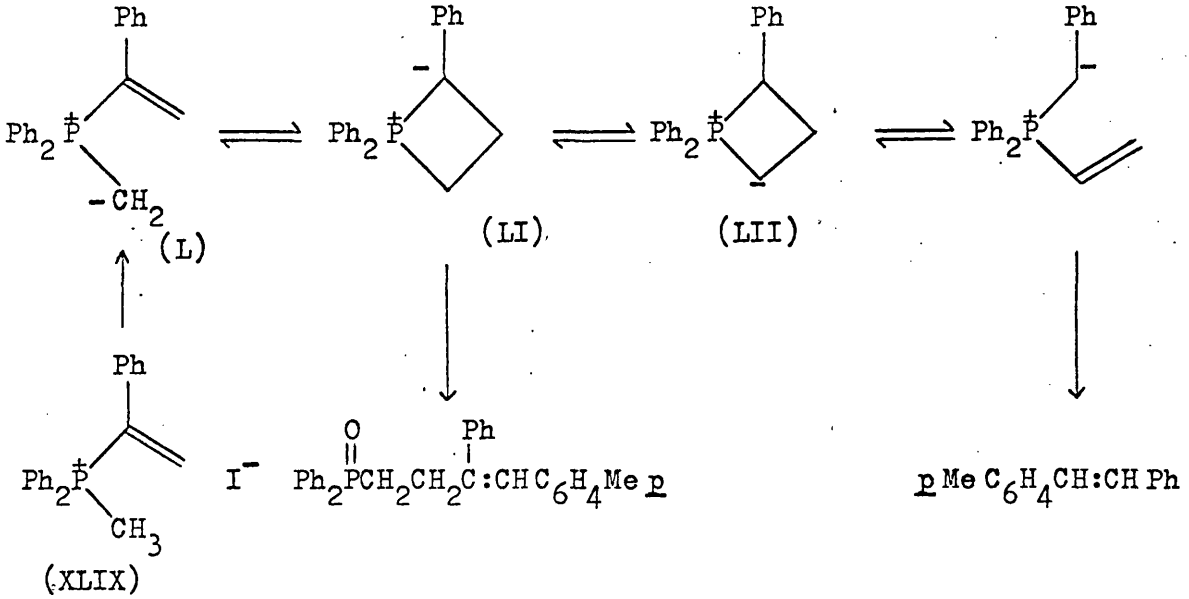


(XLVII)



(XLVIII)

In order to investigate the possible formation of a four-membered cyclic phosphorane, the ylid (L), generated from the methiodide (XLIX) of diphenyl-1-phenylvinylphosphine by reaction with n-butyllithium, was treated with p-tolualdehyde[27]. The products isolated showed that a four membered cyclic ylid (LI) had been formed[27] as indicated below:

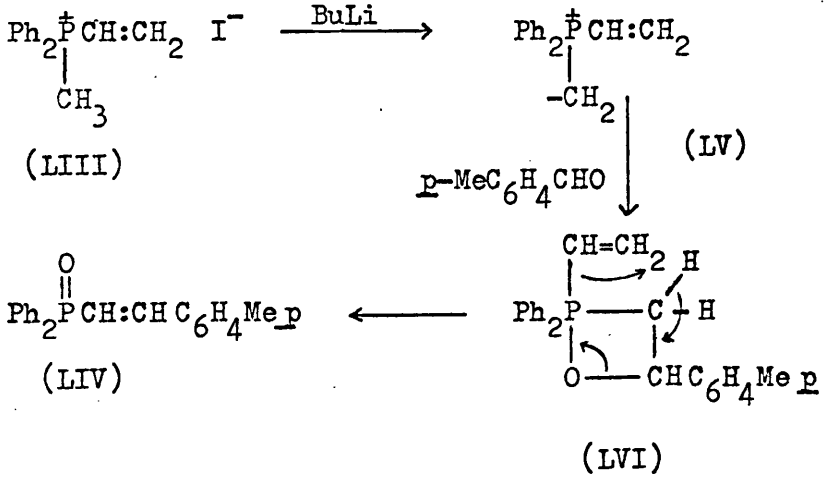


(L) (LI) (LII) (XLIX)

In a further investigation into the possibility of four-membered cyclic ylid formation by internal Michael addition, the vinyl salts already prepared, as well as m-methylbenzyldiphenyl-1-phenylvinyl phosphonium bromide, were treated with an equimolar quantity of n-butyllithium, followed by an excess of an aromatic aldehyde.

A. Methyldiphenylvinylphosphonium iodide (LIII), on treatment with butyllithium and p-tolualdehyde, gave p-methylstyryldiphenylphosphine oxide (LIV)in low yield and a polymeric oil in high yield. This polymeric oil, on alkaline hydrolysis, gave phosphine oxide (LIV). The mechanism for the formation of oxide (LIV) is probably similar to that proposed by Savage and Trippett for the reaction of diphenyl-1-phenylvinylphosphine with styrene oxide [27].

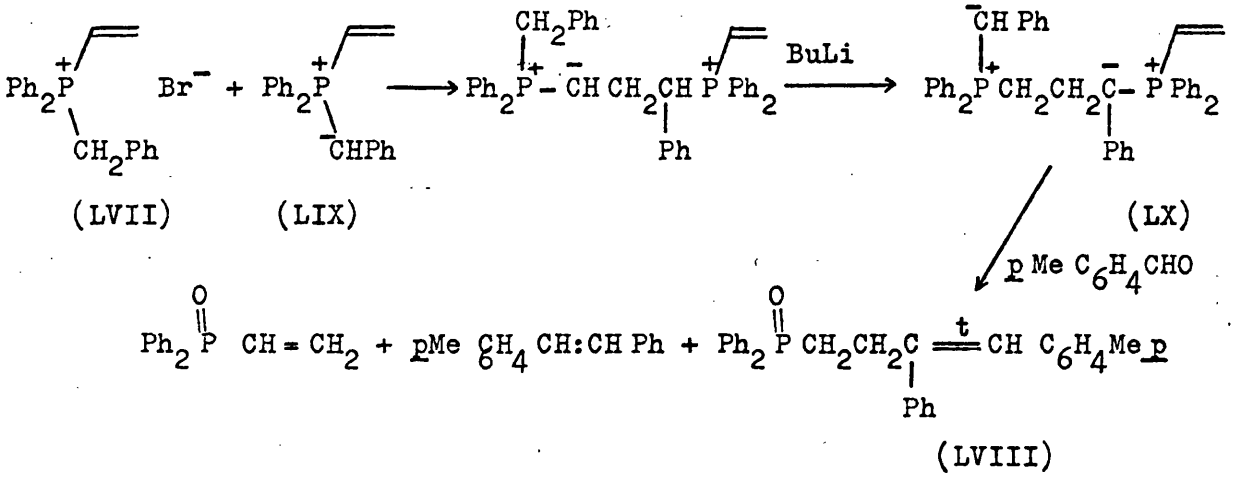
The ylid (LV) reacted with p-tolualdehyde to give the betaine (LVI), which then underwent a modified Wittig reaction. Instead of the usual four-centre rearrangement, phosphoryl double bond formation occurred synchronously with loss from the phosphorous atom of the vinyl group, which then abstracted a proton from the adjacent ∝-carbon atom of the four-membered ring.



The polymeric material produced in this reaction was presumably formed by attack of the methylene ylid (LV) on the vinyl group of a salt. Successive Michael additions of a similar nature would lead

to polymeric phosphonium salt formation.

B. Treatment of benzyldiphenylvinylphosphonium bromide (LVII) with butyllithium and p-tolualdehyde gave 4-methylstilbene, trans-1-p-tolyl-2-phenyl-4-diphenylphosphinylbut-1-ene (LVIII) and a polymeric phosphonium salt. Although the formation of phosphine oxide (LVIII) can be postulated as coming from the cyclic ylid (LI), absence of the cis isomer of (LVIII) and 4-methylstyrene, as shown by G.L.C., does not favour this pathway. A more likely mechanism would be the attack of the benzylidene ylid (LIX) on the vinyl group of the salt (LVII), followed by proton transfer to give another benzylidene ylid.

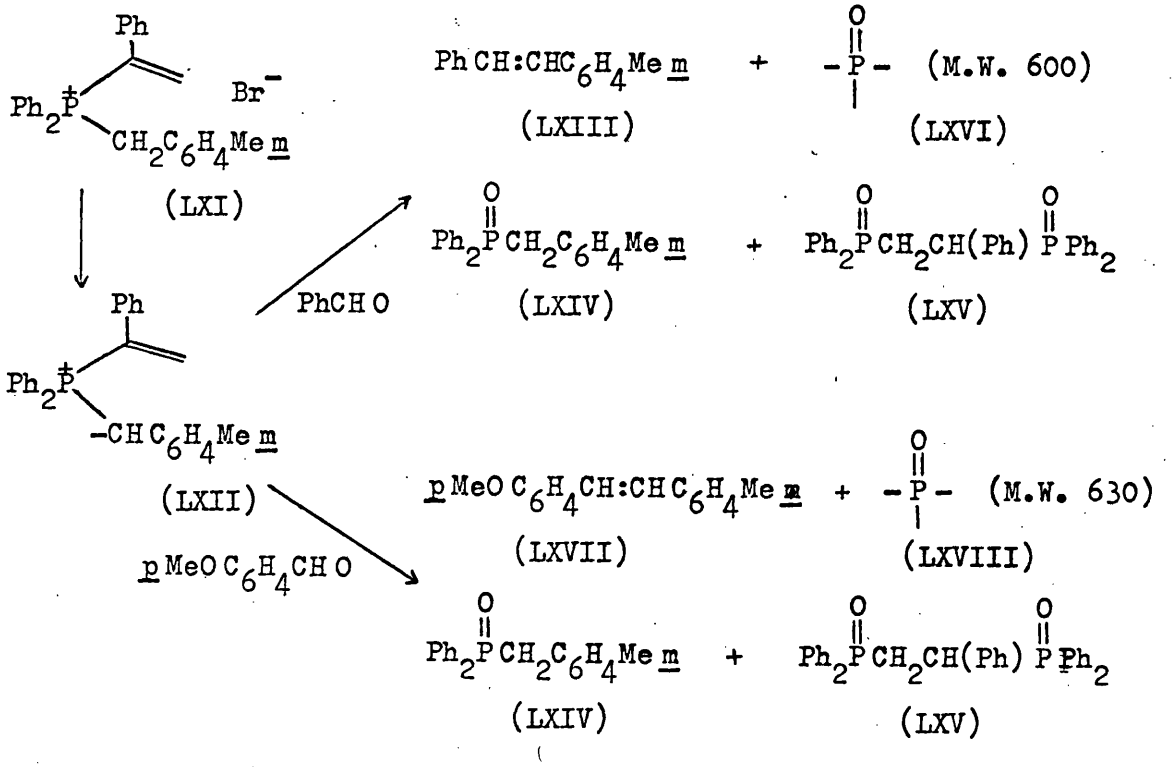


The remaining half equivalent of butyllithium would remove the other benzylic proton to give the di-ylid (LX) which subsequently reacted with the aldehyde to give the observed products, except for diphenylvinylphosphine oxide which would decompose during chromatography on alumina.

Successive addition of the ylid (LIX) to the vinyl group would lead to polymer formation. Alkaline hydrolysis of this polymeric phosphonium salt gave the trans phosphine oxide (LVIII) and 3-phenylpropyldiphenylphosphine oxide. The structure of the latter phosphine oxide was confirmed by synthesis of an authentic sample by hydrogenation of cinnamyldiphenylphosphine oxide. 3-Phenylpropyldiphenylphosphine oxide exhibited a remarkable mass spectral breakdown pattern, for the base peak

occurred at $^{m}/e$ 215. All compounds containing the diphenylphosphinyl group have, up till now, exhibited a base peak at $^{m}/e$ 201[54]. The probable reason for this phenomenon is that it is more favourable, upon electron impact, to split the molecule into $Ph_2\overset{O}{\overset{\|}{P}}CH_2^+$ and a styrene entity than it is to form $Ph_2\overset{O}{\overset{\|}{P}}^+$ and $PhCH_2CH_2CH_2$.

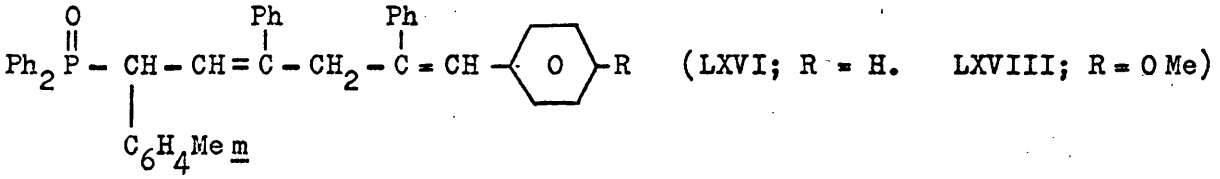
C. m-Methylbenzyldiphenyl-1-phenylvinylphosphonium bromide (LXI) was prepared by the quaternisation of diphenyl-1-phenylvinylphosphine with m-methylbenzyl bromide. The ylid (LXII) generated from this salt was treated with excess benzaldehyde. Chromatography on basic alumina gave 3-methylstilbene (LXIII), m-methylbenzyldiphenylphosphine oxide (LXIV), 1,2-bis(diphenylphosphinyl)-1-phenylethane (LXV) and a phosphine oxide (LXVI) having a molecular weight of 600.



Repeating this experiment with anisaldehyde instead of benzaldehyde gave 4'-methoxy-3-methylstilbene (LXVII) in place of (LXIII) and a phosphine oxide (LXVIII), having a molecular weight of 630, in place of oxide (LXVI). Phosphine oxides (LXIV) and (LXV) were again produced in similar yields.

The mass spectra of both oxides (LXVI) and (LXVIII) indicated the

presence of one diphenylphosphinyl group ($^{m}/e$ 201) per molecule. Replacement of benzaldehyde with anisaldehyde increased the molecular weight by 30, indicating the presence of one aldehyde residue per molecule, a result confirmed by the ^{1}H N.M.R. spectrum of oxide (LXVIII). The ^{1}H N.M.R. spectrum for both oxides showed the presence of one aromatic methyl group and one benzylic proton on a carbon adjacent to the phosphorus atom. The U.V. spectrum for oxide (LXVI) was characteristic of an α-substituted trans-stilbene [55], whilst that for the oxide (LXVIII) corresponded to an α-substituted 4^{1}-methoxystilbene. Elemental analysis of oxide (LXVI) agreed with a formula of $C_{43}H_{37}OP$. On the basis of all this data the following structure was proposed, but no satisfactory mechanism could be devised for its formation.



(LXVI; R = H. LXVIII; R = OMe)

In fact no satisfactory mechanism to account for the formation of all the products could be devised. Whatever the mechanism, however, there was no evidence for the formation of a four-membered cyclic phosphorane.

Conclusion.

No evidence for the formation of a four-membered cyclic phosphorane was obtained from the three systems studied, although Savage had observed such an occurrence. These observations have a simple explanation based upon two factors, the relative stabilities of the ylids, and the energy barrier to the formation of a four-membered ring containing a tetrahedral phosphorus atom.

In the case studied by Savage [27], a methylene ylid (L) cyclised to a benzylidene ylid (LI). Thus it can be concluded that the gain in stability on forming a more stable ylid overcomes the energy barrier to the formation of a strained four membered ring.

(L) (LI) (LXIX)

However, the cyclisation of methylenediphenylvinylphosphorane (LXIX: R = R^1 = H) to another methylenephosphorane would be an unfavourable process, as there would be no gain in ylid stability to overcome the energy barrier to cyclisation.

A similar case applies to the benzylidene ylid (LXIX; R = Ph, R^1 = C_6H_4Me m) whose cyclisation would produce another benzylidene ylid.

In the case of benzylidenediphenylvinylphosphorane (LIX), (LXIX; R = H, R^1 = Ph), this cyclisation process would be very unfavourable as it would convert a relatively stable benzylidenephosphorane to an unstable methylenephosphorane. Thus there would be a loss in ylid stability as well as the energy barrier to cyclisation to overcome.

Alkaline Hydrolysis of Vinylphosphonium Salts and their Derivatives.

During this investigation into the preparation and properties of vinylphosphonium salts, several salts of unknown composition were produced which were subjected to alkaline hydrolysis in the course of elucidation of their structure. In order to obtain more information on the reactions of these salts, a number of vinyl and β-substituted ethylphosphonium salts were subjected to alkaline hydrolysis.

A limited discussion on the mechanism of alkaline hydrolysis will be given here, a more complete review will be given later in this thesis.

A quaternary phosphonium salt decomposes on alkaline hydrolysis to a tertiary phosphine oxide and a hydrocarbon [56]. Hydrolysis of most

acyclic phosphonium salts have been found to be second order in hydroxyl and first order in the salt [57, 58]. The first step in the mechanism is believed to be the reversible attack of hydroxyl ion on the phosphorus atom to give a pentacoordinate species. This is followed by the removal of the hydroxyl proton by a second hydroxyl ion, coupled with loss of the group which is most stable as the anion. This anion is then protonated from the aqueous medium to give a hydrocarbon.

Several groups of workers have investigated the ease of elimination of groups in the alkaline hydrolysis of phosphonium salts [59, 60] and from their work the following order for the ease of elimination of different groups could be obtained:

p-nitrobenzyl > allyl, benzyl > α-naphthyl > phenyl > β-phenethyl > methyl > higher alkyls.

a) Bis-Phosphonium Salts.

The alkaline hydrolyses of several bis-phosphonium salts were found to conform to the observations of Brophy and Gallagher[61], who devised an empirical relationship between a bis-salt and its hydrolysis products. This relationship was devised for symmetrical bis-salts and the benzyl group, when present, was the group most easily lost on hydrolysis. A diagramatic representation of this relationship is as follows:

$R_3\overset{+}{P}CH_2CH_2\overset{+}{P}R_3$
$2X^-$

a) $4R = PhCH_2$; $(PhCH_2)_2R\overset{+}{P}CH_2CH_2\overset{+}{P}R(CH_2Ph)_2 \xrightarrow{OH^-} (PhCH_2)R\overset{O}{\overset{\|}{P}}CH_2CH_2\overset{O}{\overset{\|}{P}}R_{(CH_2Ph)}$

b) $2R = PhCH_2$; $(PhCH_2)R_2\overset{+}{P}CH_2CH_2\overset{+}{P}R_2(CH_2Ph) \xrightarrow{OH^-} R_2\overset{O}{\overset{\|}{P}}CH_2CH_2\overset{O}{\overset{\|}{P}}R_2 +$

$R_2\overset{O}{\overset{\|}{P}}CH_2Ph + R_2PCH_2Ph + C_2H_4 + PhCH_3$

c) $R \neq PhCH_2$; $R_3\overset{+}{P}CH_2CH_2\overset{+}{P}R_3\ 2X^- \xrightarrow{OH^-} R_3P + R_3P=O + C_2H_4$

The alkaline hydrolysis of two bis-phosphonium salts described earlier in this thesis were found to conform to this hypothesis.

Ethylenebis(dibenzylphenylphosphonium) dibromide (XXXVI) prepared by the treatment of β-bromophenetole with impure dibenzylphenylphosphine, gave on hydrolysis 1,2-bis (benzylphenylphosphinyl)ethane and constituted an example of type (a).

The hydrolysis of the bis-salt (XXXIII) from the quaternisation of diphenylvinylphosphine with benzyl bromide in methanol-propionaldehyde gave 1,2-bis(diphenylphosphinyl)ethane and benzyldiphenylphosphine oxide. This reaction was an example of type (b) except that one benzyl had been replaced by a vinyl group, which is also a fairly good leaving group relative to phenyl.

$$(PhCH_2)Ph_2\overset{+}{P}CH_2CH_2\overset{+}{P}Ph_2(CH=CH_2)\quad 2Br^- \xrightarrow{^-OH} Ph_2\overset{O}{\overset{\|}{P}}CH_2CH_2\overset{O}{\overset{\|}{P}}Ph_2 + Ph_2\overset{O}{\overset{\|}{P}}CH_2Ph$$

(XXXIII)

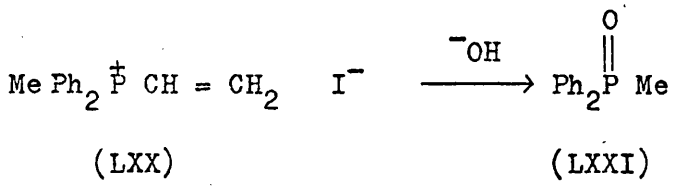
In this experiment the phosphines were oxidised and diphenylvinylphosphine oxide decomposed on the alumina column.

b) Mono-Phosphonium Salts.

A survey of the literature on the hydrolysis of vinyl, β-substituted ethyl and bis-phosphonium salts revealed that in many cases neither the strength of the alkali nor the nature of the medium used (aqueous or aqueous ethanolic) was given. Also where gas evolution was postulated only a few reports of attempts to trap the gas were found. As will be seen from the results obtained, the strength of alkali and the nature of the medium used can have a profound effect upon the course of the reaction.

Methyldiphenylvinylphosphonium Iodide.

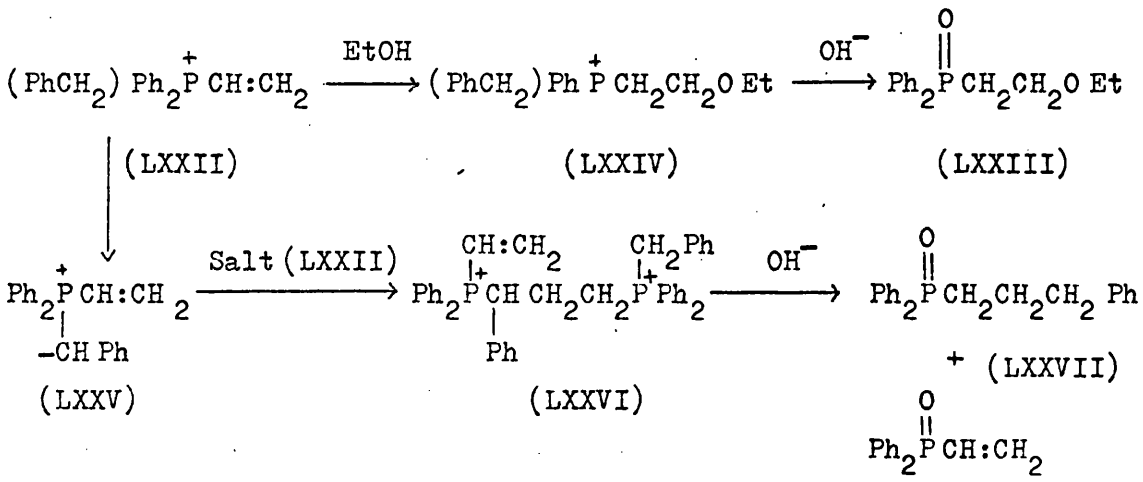
Hydrolysis of methyldiphenylvinylphosphonium iodide (LXX) in 2N aqueous sodium hydroxide solution gave methyldiphenylphosphine oxide (LXXI). Thus it would appear that the vinyl anion was lost more readily than the phenyl anion.



(LXX) (LXXI)

Benzyldiphenylvinylphosphonium Bromide.

Hydrolysis of benzyldiphenylvinylphosphonium bromide (LXXII) in aqueous ethanolic sodium hydroxide solution gave 2-ethoxyethyl-diphenylphosphine oxide (LXXIII) by Michael addition of ethanol to the double bond followed by loss of a benzyl anion from the intermediate salt (LXXIV) on hydrolysis. Toluene was certainly produced in this reaction as the bromine trap yielded 2,4,5-tribromotoluene.



(LXXII) (LXXIV) (LXXIII)

(LXXV) (LXXVI) + (LXXVII)

However, when the hydrolysis of this salt was carried out in 2N aqueous sodium hydroxide solution, diphenyl-3-phenylpropylphosphine oxide (29%) (LXXVII), diphenylvinylphosphine oxide (22%) and a polymeric oil were isolated. Formation of the phosphine oxide (LXXVII) might at first appear to be by the migration of a benzyl group to the β-carbon atom of the vinyl group. A more plausible explanation would be that in aqueous alkaline solution, a small quantity of benzylidene ylid (LXXV) was present. This ylid would add to the vinyl group of the

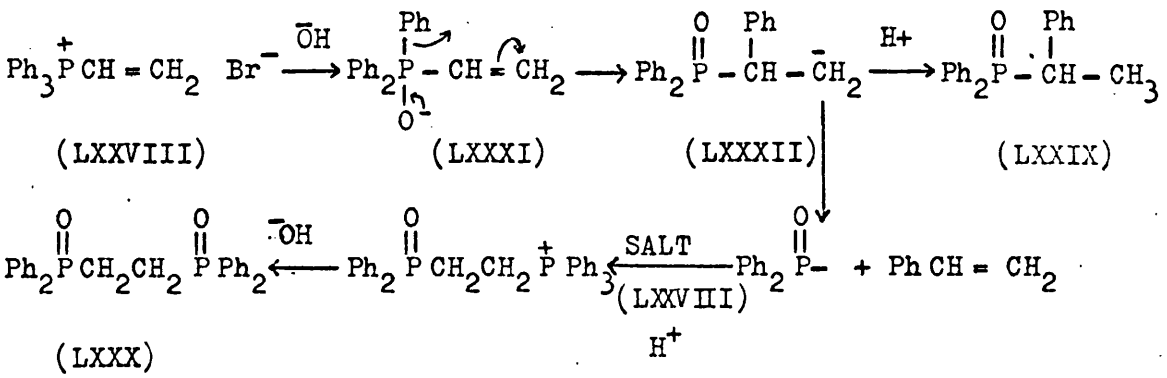
unreacted salt (LXXII) which on protonation would give the bis-salt (LXXVI). Hydrolysis of this bis-salt would give diphenyl-3-phenylpropylphosphine oxide (LXXVII) and diphenylvinylphosphine oxide. However, successive addition of ylid (LXXV) to the salt (LXXVI) would lead to polymer formation.

Triphenylvinylphosphonium Bromide.

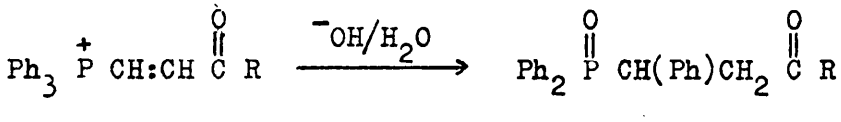
Hydrolysis of triphenylvinylphosphonium bromide (LXXVIII) in aqueous ethanolic sodium hydroxide solution gave 2-ethoxyethyldiphenylphosphine oxide by Michael addition of ethanol to the vinyl group, followed by loss of a phenyl group on hydrolysis.

When the hydrolysis of this salt was carried out in 2N aqueous sodium hydroxide solution, triphenylphosphine (a trace), 1-phenylethyldiphenylphosphine oxide (LXXIX) (7%), triphenylphosphine oxide (7%) and 1,2-bis(diphenylphosphinyl)ethane (LXXX) (83%) were produced. G.L.C. analysis of the reaction mixture showed the presence of styrene which led to the postulation of the following mechanism.

Initial attack of hydroxyl ion at phosphorus gave the intermediate (LXXXI), in which migration of a phenyl anion from phosphorus to the α-carbon atom of the vinyl group took place to give the carbanion (LXXXII). Now, either protonation took place to give 1-phenylethyldiphenylphosphine oxide (LXXIX) or elimination of styrene took place to give the diphenylphosphinyl anion. Attack by this anion upon the vinyl group of the salt (LXXVIII) gave a phosphine oxide-phosphonium salt which on hydrolysis gave 1,2-bis(diphenylphosphinyl)ethane (LXXX).

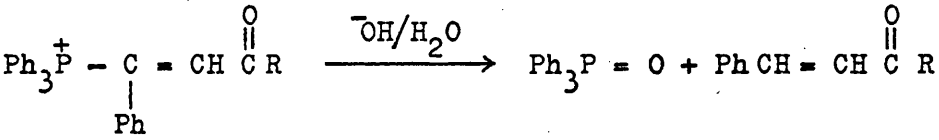


Several similar examples of phenyl migration in the alkaline hydrolysis of vinylphosphonium salts have been reported. Alkaline hydrolysis of the β-acylvinyl salt (LXXXIII) proceeded with phenyl migration to the α-carbon atom[21].

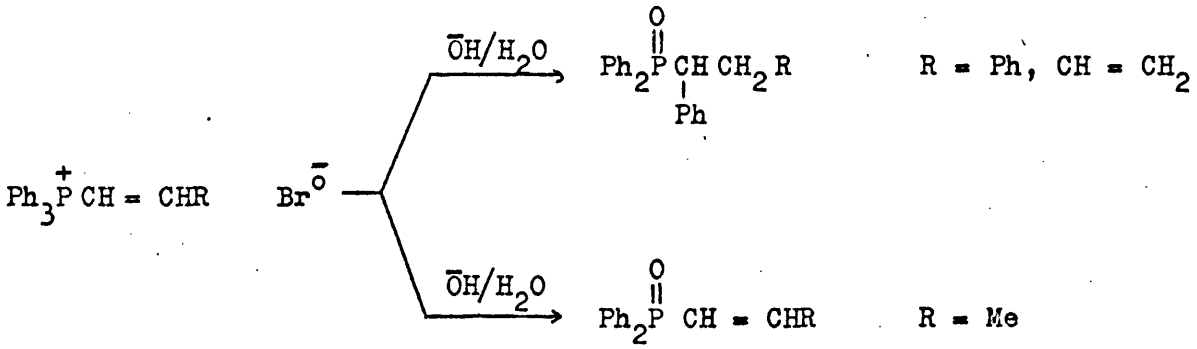


(LXXXIII)

However, when an α-phenyl-β-acylvinylphosphonium salt was hydrolysed, no phenyl migration was observed[26] as the α-phenylvinyl anion was such a very good leaving group[27].



Brophy, Freeman and Gallagher studied the alkaline hydrolysis of styryl-, propenyl- and butadienyl-phosphonium salts (LXXXIV)[25] and found that migration of a phenyl anion from phosphorus to the α-carbon atom occurred only when the group R, on the β-carbon of the vinyl group, was able to stabilise the incipient carbanion. Thus migration occurred when the group R was phenyl or vinyl, but not when R was methyl.



These workers did not observe the formation of substituted styrenes of the type Ph CH : CHR (R = Ph, $-CH = CH_2$), so it would appear that the hydrolysis of the unsubstituted vinyl salt (LXXVIII) was in the intermediate zone between no migration whatsoever and complete migration with

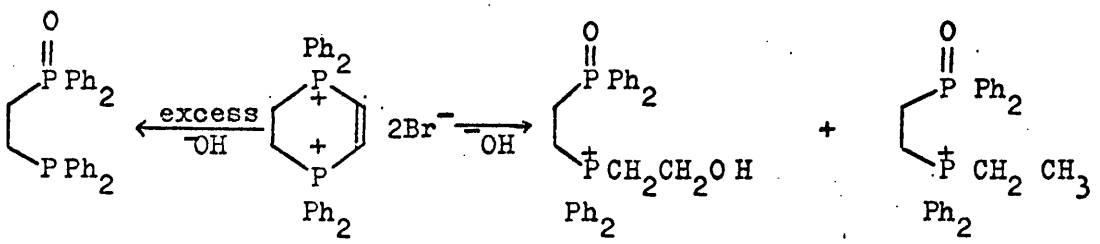
no other products formed from the intermediate carbanion.

Triphenylphosphine oxide was produced by the normal hydrolysis of salt (LXXVIII) with the loss of the vinyl group as ethylene. The mechanism for the formation of triphenylphosphine is not known. Certainly, it was not formed by addition of water to the vinyl group of the salt (LXXVIII) to give 2-hydroxyethyltriphenylphosphonium bromide, followed by removal of a proton from the β-carbon atom and elimination of triphenylphosphine from the betaine (LXXXV), for it is known [62, 63] and has been confirmed that the alkaline hydrolysis of 2-hydroxyethyltriphenylphosphonium bromide under these conditions gave 2-hydroxyethyldiphenylphosphine oxide and a little triphenylphosphine oxide, but no trace of triphenylphosphine.

$$\underset{\text{(LXXVIII)}}{Ph_3\overset{+}{P}CH=CH_2\ Br^-} \xrightarrow{H_2O} Ph_3\overset{+}{P}CH_2CH_2OH\ B\bar{r} \xrightarrow{\bar{O}H} \underset{\text{(LXXXV)}}{Ph_3\overset{+}{P}-CH_2-\overset{-}{C}HOH} \longrightarrow Ph_3P + (CH_2CHOH)$$

Also it was found that although 2-hydroxyethyltriphenylphosphonium bromide was produced in 91% yield when the vinyl salt (LXXVIII) was treated with an equimolar quantity of 0.01N aqueous sodium hydroxide, this addition was not observed under the conditions of hydrolysis of this salt (LXXVIII).

Addition of water to a vinylphosphonium salt intermediate during hydrolysis has been reported[61], but the hydroxide ion concentration was as low as possible for hydrolysis to occur[64]. Treatment of 1,1,4,4-tetraphenyl-1,4-diphosphoniacyclohexene dibromide (LXXXVI) with excess alkali gave ethylene bis(diphenylphosphine) monoxide, whereas slow addition of dilute alkali to the salt (LXXXVI) gave two phosphonium salts, one of which (LXXXVII) was produced by the addition of water to the intermediate vinyl salt.

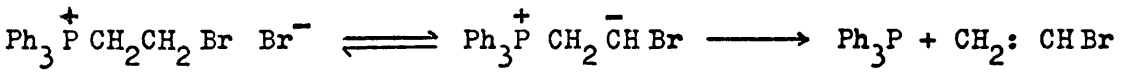


(LXXXVI) (LXXXVII)

The alkaline hydrolyses of 2-phenoxyethyltriphenylphosphonium bromide gave the same products in similar yields as the corresponding hydrolyses of triphenylvinylphosphonium bromide (LXXVIII), except that for the hydrolysis in aqueous alkaline media, phenol was isolated in addition to the other products. The first step in this reaction was presumably the base catalysed elimination of phenol to give the vinyl salt (LXXVIII) which then hydrolysed in the manner already shown.

2-Bromoethyltriphenylphosphonium bromide.

One reaction which exemplified the dependency upon the nature of the medium was the hydrolysis of 2-bromoethyltriphenylphosphonium bromide (LXXXVIII). In 2N sodium hydroxide and ethanol in a 3:2 ratio, triphenylphosphine (75%) was the only isolated product. A possible mechanism would be the removal by base of a proton from the carbon adjacent to the bromine followed by elimination of triphenylphosphine from the intermediate betaine (LXXXIX).



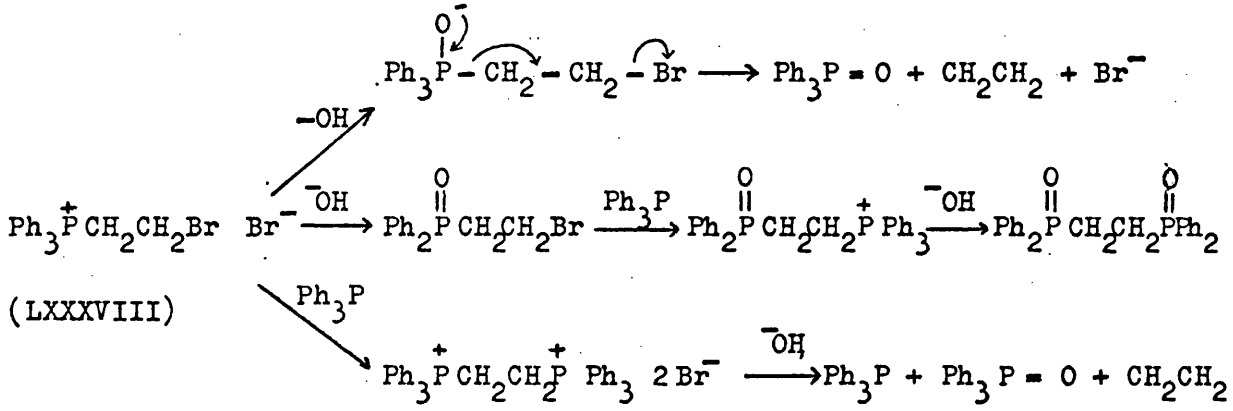
(LXXXVIII) (LXXXIX)

However, no derivatives of vinyl bromide were detected in the bromine trap, so it might appear that either this mechanism is incorrect or that the trap was insensitive. The latter factor is believed to be the correct one, for in a range of experiments, it was found that low boiling unsaturated compounds were not trapped whereas benzene and toluene were trapped as p-dibromobenzene and 2,4,5-tribromotoluene respectively.

A similar mechanism has been proposed for the hydrolysis of

2-acetoxyethyltriphenylphosphonium bromide in concentrated sodium hydroxide solution[62], where triphenylphosphine was isolated in 95% yield.

When the hydrolysis of this salt (LXXXVIII) was carried out in 2N aqueous sodium hydroxide solution, triphenylphosphine (43%), triphenylphosphine oxide (34%) and 1,2-bis(diphenylphosphinyl)ethane (21%) were isolated. The formation of triphenylphosphine can be postulated as in the previous hydrolysis. However, this reaction was now in competition with one or more other processes. Some of these possible processes are set out in the reaction scheme below.



The formation of triphenylvinylphosphonium bromide by base catalysed elimination of hydrogen bromide from the salt (LXXXVIII) was believed not to occur as 1-phenylethyldiphenylphosphine oxide could not be detected.

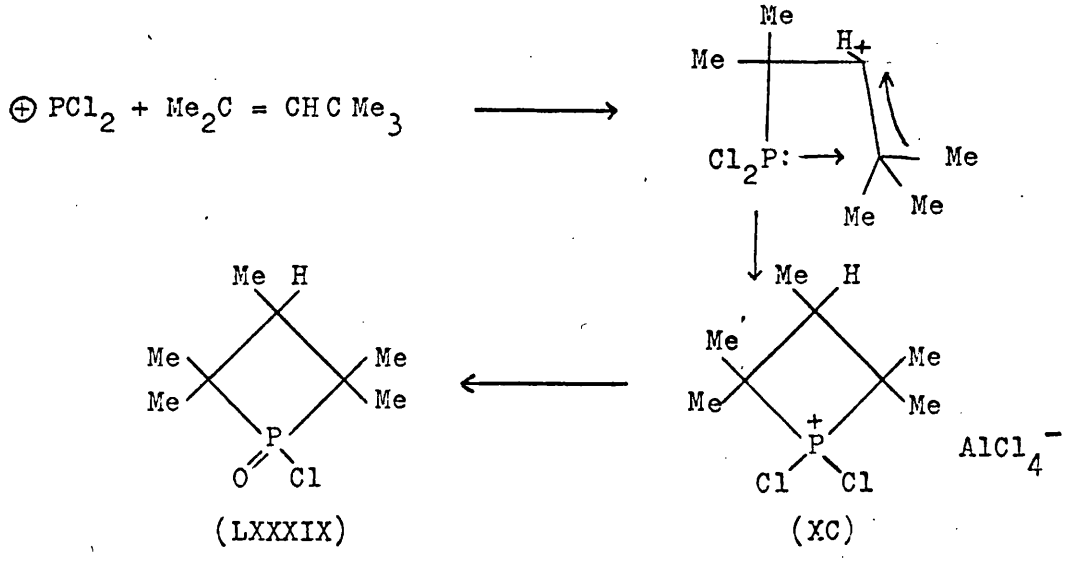
Conclusion.

The alkaline hydrolyses of vinyl- and β-substituted ethylphosphonium salts were more complex than originally anticipated. Although it would appear that for a normal hydrolysis, the unsubstituted vinyl group would lie between phenyl and benzyl on the scale of ease of loss, this is not the usual occurrence. Due to the unsaturated nature of this group and the positive centre to which it is attached, attack by nucleophiles takes place readily which means that during hydrolysis more complicated reactions occur than would at first be expected.

Phosphetanes.

A phosphetane is a heterocyclic compound containing a four membered ring consisting of one phosphorus and three carbon atoms. Although many examples of four membered phosphorus heterocycles are known, especially in the fields of phosphine imide dimers and as postulated intermediates in the Wittig olefin synthesis, there are few reports of phosphetanes.

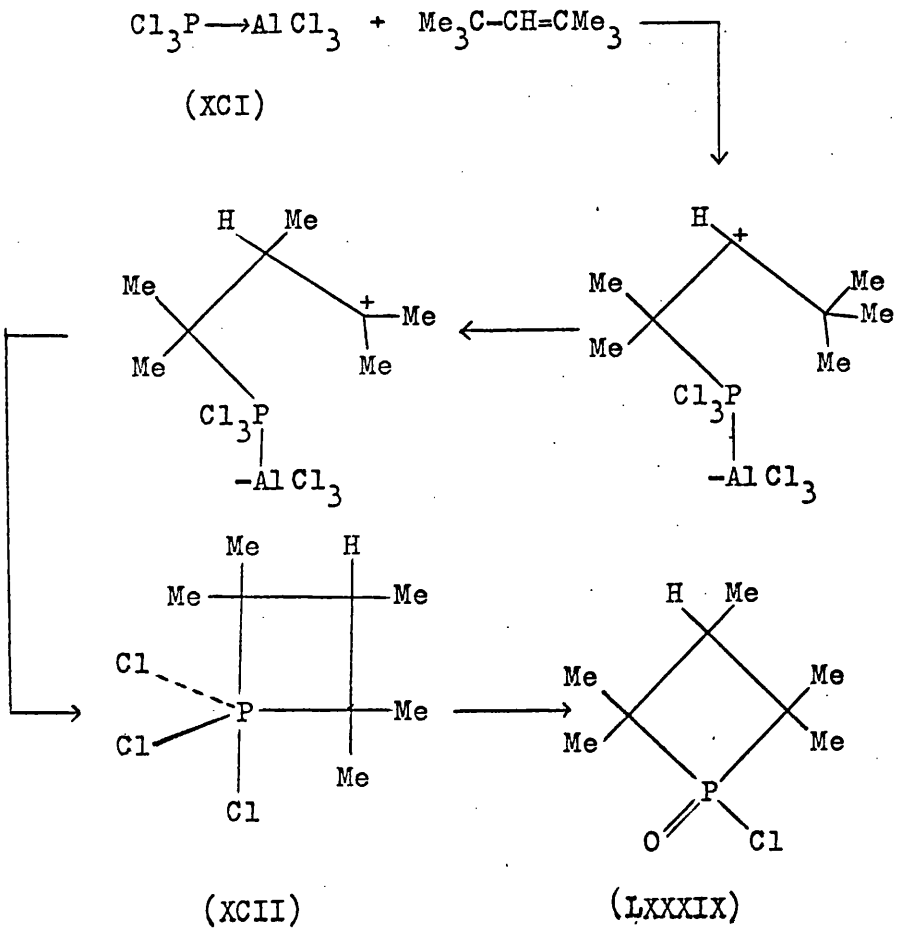
The first satisfactory preparation was found by Jungermann and McBride[65] during a systematic investigation into the reactions of phosphorus trichloride with olefins. They found that the addition of a particular olefin, namely 2,4,4-trimethylpent-2-ene, to an equimolar mixture of phosphorus trichloride and aluminium chloride gave, on treatment with water, the cyclic acid chloride (LXXXIX). They proposed that, in the presence of aluminium chloride, phosphorus trichloride formed the species $^{+}PCl_2$, which attacked the olefin to give a secondary carbonium ion. Methyl migration to give a tertiary carbonium ion was followed by, or occurred synchronously with, cyclisation to the phosphetanium salt (XC). Decomposition of (XC), on treatment with water, gave the cyclic acid chloride (LXXXIX).



(LXXXIX) (XC)

The possible weakness of this mechanism is that a strained four-membered ring containing a tetrahedrally coordinated phosphorus atom

is formed in the cyclisation step. Although formation of the species $\oplus P Cl_2$ is possible, the most likely species to be formed is the donor-acceptor complex (XCI) where the phosphorus is positive and the aluminium is negative in character. This species (XCI) reacts with the olefin, giving a secondary carbonium ion in which methyl migration occurs to give a tertiary carbonium ion. Ring closure then takes place to give a pentacoordinate phosphorane (XCII) in which the four membered ring lies in an unstrained conformation spanning a bond angle of 90° at phosphorus. Decomposition of the trichlorodialkyl-phosphorane (XCII) would then give the acid chloride (LXXXIX).

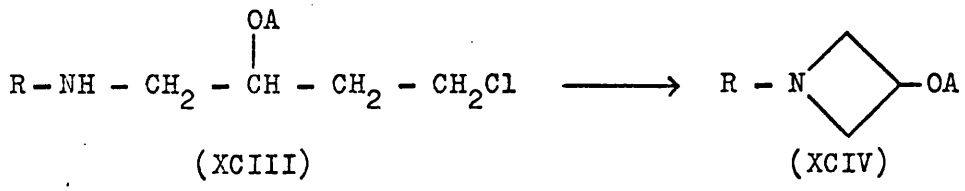


This synthesis has been adapted by Hawes and Trippett[66,67] and by Cremer and Chorvat[68] for the use of other t-butyl and isopropyl-olefins with alkyl- and aryl-phosphonous dichlorides. In this way the number of C-methyl substituents on the ring could be varied between three and five, and groups other than chlorine could be placed on the phosphorus

atom. Substitution of chlorine for other groups on phosphorus could be carried out by treatment of the cyclic acid chloride with a Grignard reagent or with an equimolar quantity of the appropriate organolithium compound[66,69].

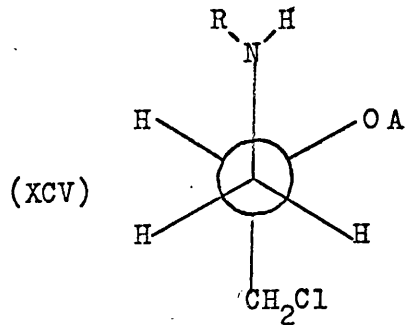
However, this synthesis is restrictive in that at least one α-carbon atom of the ring always bears two methyl groups and in some cases the molecules are very sterically crowded. In fact Jungermann and McBride proposed that cyclisation occurred only with highly substituted olefins for this very reason.

A more general synthesis of phosphetanes, where the ring bears far fewer substituents, can be developed using the proposals put forward for the synthesis of azetidines, the nitrogen analogues of phosphetanes[70-72].

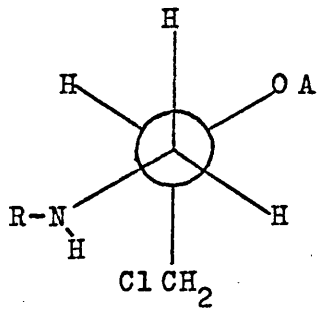


(XCIII) (XCIV)

Gaertner[71] found that the intermediate (XCIII; A = H), from the action of a primary amine on epichlorohydrin, cyclised readily to the azetidine (XCIV) when the group R was fairly bulky. Further work by Gaj and Moore showed that in a reaction in which compound (XCIII; A = CH_2OCH_3) was an intermediate, cyclisation would occur even when the group R was small. Thus the cyclisation process depended upon the steric bulk of the groups A and R. When the steric bulk of A and R was small, cyclisation would not occur because the preferred conformation of (XCIII) was as shown in (XCV) with the two groups required to take part in cyclisation lying <u>trans</u> diaxial. However, when the total steric bulk was larger, the preferred conformation (XCVI) was such that cyclisation would take place more readily.

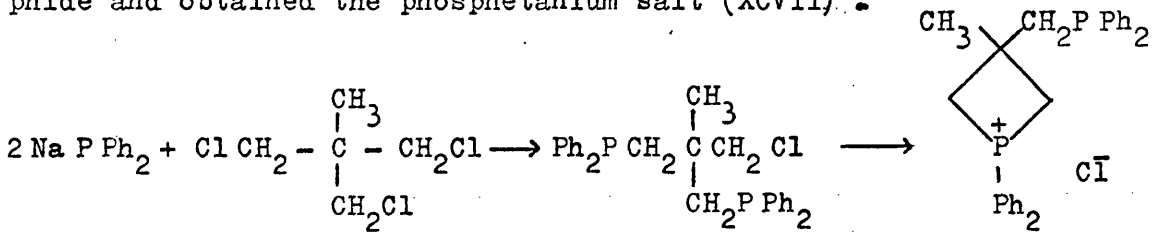


(XCV)



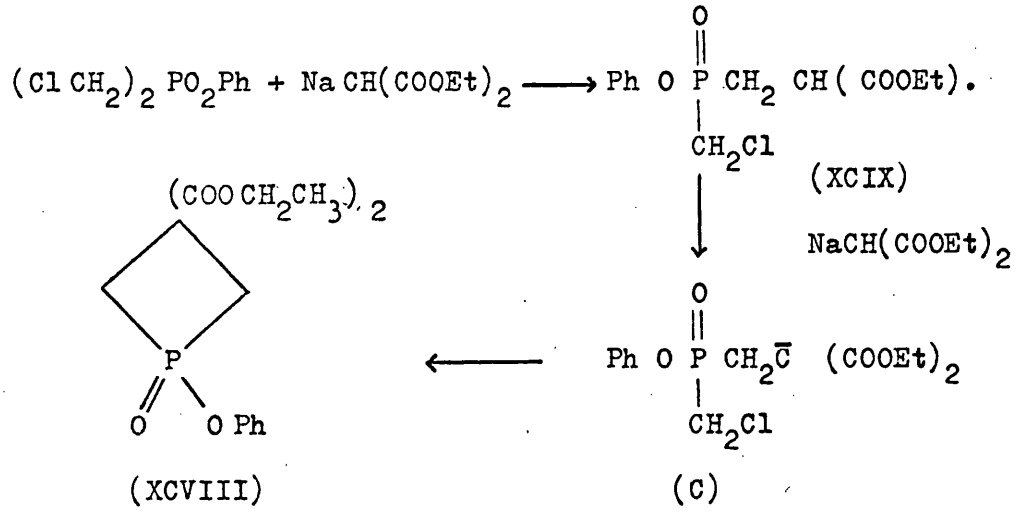
(XCVI)

Two examples in organophosphorus chemistry which obey this theory have recently been reported. Berglund and Meek[73] treated 2-chloromethyl-1-3-dichloro-2-methylpropane with sodium diphenylphosphide and obtained the phosphetanium salt (XCVII).



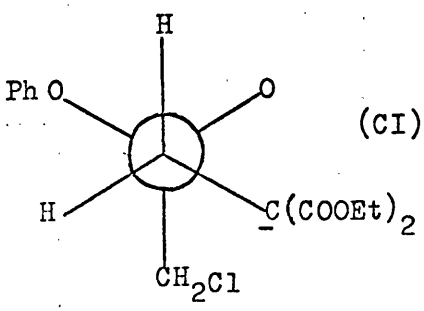
(XCVII)

The second example showed that cyclisation need not occur at the phosphorus centre. Treatment of phenyl bis(chloromethyl)phosphinate with two equivalents of sodiodiethylmalonate gave the substituted phosphetane (XCVIII)[74].



(XCVIII)

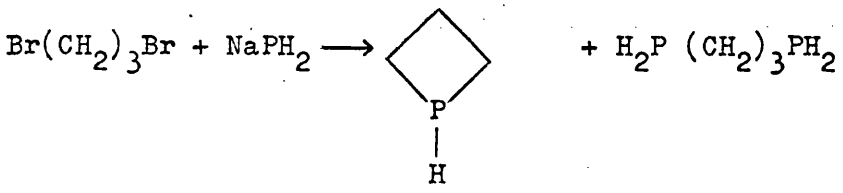
(C)



(CI)

Presumably the phosphinate condensed with the first mole of sodiomalonicester to give the species (XCIX) from which a proton was removed by the second equivalent of sodiomalonic ester, to give the species (C). This species would prefer to exist in the conformation (CI) in which cyclisation took place to give the phosphetane (XCVIII).

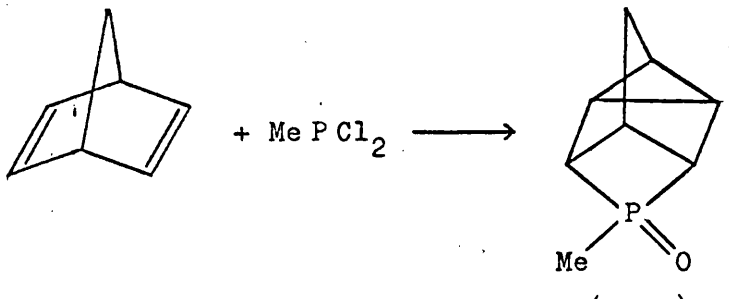
The simplest possible phosphetane has been prepared by Wagner[75] using vacuum techniques at low temperatues. Treatment of 1,3-dibromopropane with sodium phosphide gave two products, the phosphetane (CII) and the acyclic biphosphine.



(CII)

The phosphinic acid analogue of the phosphetane (CII) has been prepared in microscopic yield by Kosolapoff[76] from 3-bromopropanedichlorophosphine. All other attempts at preparing phosphetanes by the action of phosphines and phosphides on 1,3-dihalopropanes[77] and dialdehydes[78] as well as attempted self quaternisations of 3-halopropylphosphines[77] have been unsuccessful.

The only other successful phosphetane synthesis was by Green [79], who prepared the highly substituted phosphetane (CIII) by the reaction of methylphosphonous dichloride with norbornadiene.



(CIII)

Attempts to extend this preparation by use of other chlorophosphines were unsuccessful, as were attempted 1,4-cycloaddition reactions of phosphines with cyclopentadiene[66, 80, 81].

The Alkaline Hydrolysis of Phosphonium Salts.

A quaternary phosphonium salt decomposes on alkaline hydrolysis to give a tertiary phosphine oxide and a hydrocarbon. Since Michaelis observed[82] that tolyl and phenyl groups were lost more easily than alkyl groups, fairly extensive investigations have been carried out, notably by Meisenheimer[56] and Ingold[59], from which the following order for the ease of loss of groups was drawn up:-

Allyl, benzyl > phenyl > methyl > β-phenethyl > ethyl and higher alkyls.

More recent work by Horner[60] on tetraarylphosphonium salts has shown that aryl groups containing electron withdrawing substituents are more easily lost than phenyl, whereas aryl groups bearing electron releasing substituents are less easily lost than phenyl. A similar pattern has been found for substituted benzyl groups in the hydrolysis of substituted-benzyltribenzylphosphonium salts[83]. Therefore the group most easily lost on alkaline hydrolysis of that which is most stable as an anion, and vice versa, a view confirmed by other investigations[57, 84].

When the salt had no single group which was the most easily lost, then hydrolysis yielded a mixture of phosphine oxides and their corresponding hydrocarbons[60, 85]. When tetraalkylphosphonium salts were hydrolysed, where the alkyl groups were "higher n-alkyls, the content of the hydrocarbon products became statistically dependent upon the groups present. Fox example, ethyltri-n-propylphosphonium hydroxide gave 23% ethane and 77% propane, whilst triethyl-n-propylphosphonium hydroxide gave 73% ethane and 27% propane[59].

It has also been found that the ease of loss of a group was partially dependent upon the nature[83] and the steric bulk[106] of the other groups attached to the phosphorus atom.

Kinetics and Mechanism.

Kinetic studies on the alkaline hydrolysis of phosphonium salts have shown that almost all are third order processes, first order in the concentration of phosphonium salt and second order in the concentration of hydroxyl ion[57, 58, 83-6]. The exceptions to this rate law occurred when the leaving group was a very stable anion, such as p-nitrobenzyl[83] and 1,4-diphenyl-1,3-butadienyl anion[87]. These two groups were lost much more readily than benzyl and the hydrolyses were first order in the concentration of phosphonium salt, but only first order in the concentration of hydroxyl ion.

The mechanism proposed[57] to accommodate the third order dependence was essentially the same as that originally put forward by Ingold[59].

$$R_4\overset{+}{P} + \bar{O}H \rightleftharpoons R_4P\dot{O}H \overset{\bar{O}H}{\rightleftharpoons} R_4P-O^- \longrightarrow R_3P=O + R^- \quad -1$$

(CIV)

$$R^- + H_2O \longrightarrow RH + \bar{O}H$$

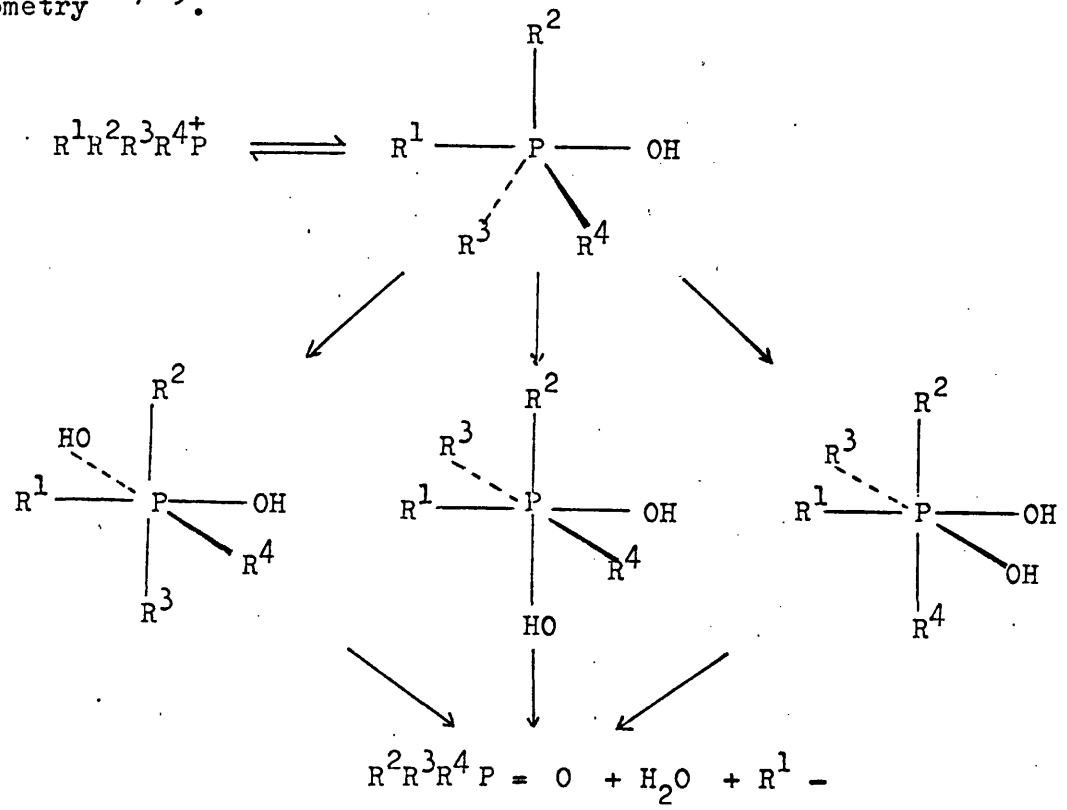
This involved a fast reversible addition of hydroxide ion to the positive phosphorus atom giving a pentacoordinate species (CIV). The second step was the fast reversible formation of the conjugate base of this species. The third step was the slow, rate-determining formation of the phosphine oxide and a carbanion. The final step was the abstraction of a proton from the aqueous medium by the carbanion.

Other mechanisms have been proposed, of which two are feasible. The first, mentioned in a review by McEwen[88], is a compressed form of the above mechanism, whereby the removal of a proton from (CIV) by the second hydroxyl ion was synchronous with the loss of the anion and the formation of the phosphine oxide.

$$R_4\overset{+}{P} + \bar{O}H \rightleftharpoons \underset{\substack{HO^{\sim}H \\ \text{(CIV)}}}{R-\overset{\overset{R}{|}}{\underset{\underset{O}{|}}{P}}\overset{R}{\underset{R}{<}}} \longrightarrow R^- + H_2O + R_3P=O$$

This mechanism satisfies the third order rate dependence very well, better in fact than the previous mechanism where the rate of formation of (CIV) is required to be similar or slightly greater than the rate of conjugate base formation.

The other mechanism involves attack of the second hydroxyl ion on an edge of the trigonal bipyramidal intermediate (CIV) between two equatorial groups to give one or more of the three possible octahedral species. Collapse of these species with simultaneous loss of the carbanion and water would give a phosphine oxide with the correct geometry[88, 89].



Stereochemistry.

The alkaline hydrolysis of the separate enantiomers of benzylethylmethylphenylphosphonium iodide has been reported as being 100% stereospecific[8, 90, 94]. The oxide obtained from the alkaline hydrolysis of this salt was found to have an optical rotation exactly opposite to that obtained from the Wittig reaction on the same enantiomer of the salt. Thus, as the Wittig reaction proceeds with retention of configuration, so the alkaline hydrolysis must be proceeding with complete inversion of configuration at phosphorus.

This stereochemical result has been confirmed using the optical enantiomers of benzylmethyl-n-propylphenylphosphonium bromide. The phosphine oxide from cathodic reduction of the salt followed by oxidation was found to have the same sign of rotation as the oxide from the Wittig reaction, but the opposite sign to that oxide obtained from alkaline hydrolysis[91 - 93].

All three possible mechanisms are compatible with inversion of configuration at the phosphorus atom. However, for a full discussion on the stereochemistry of the alkaline hydrolysis of phosphonium salts, two factors must be considered (1) the geometry of the pentacoordinate intermediate and (2) the positions of entry of the hydroxyl ion and departure of the anion.

(1) Geometry of the Intermediate.

Several geometrical structures are possible for a compound of the type MX_5[95]; however, the two most acceptable candidates for a pentacoordinate phosphorus compound are the trigonal bipyramid and the tetragonal pyramid[94-96]. Structure determinations by X-Ray crystallographic methods have recently been carried out on a number of stable pentacoordinate phosphoranes and all were found to have a trigonal bipyramidal structure[97 - 100]. Consequently, it has been assumed that the phosphorane intermediate (CIV) in an alkaline hydrolysis would also be trigonal bipyramidal. However, the energy difference between the two structures has been reported as 1.5 k.cal/mole[101], a fairly small figure, which means that interchange between these two structures could take place provided that the energy barrier to the interchange was not too great. Evidence for the occurrence of this interchange has been furnished in work on optically active ate complexes[101] and also in ^1H N.M.R. studies to investigate pseudorotation in phosphoranes[102].

(2) Position of Entry and Loss of Groups.

There are two modes of attack for the hydroxyl anion upon the tetrahedral phosphonium cation, attack on a face and attack on an edge of a tetrahedron[94]. Attack on the face of a tetrahedron is referred to as apical attack, denoted (a), for the attacking group takes up an apical position of the trigonal bipyramid initially formed. The equatorial positions are occupied by the three groups which bounded the face under attack. Attack on an edge of a tetrahedron is equatorial attack (e), for the attacking group occupies an equatorial position in the initially formed trigonal bipyramid. The two groups defining the edge under attack occupy the apical positions.

It is theoretically possible for a group to be lost from either an apical or an equatorial position of the trigonal bipyramidal intermediate. The stereochemistry of the overall reaction is governed by the position of entry and exit of groups, as given in the following table:

Stereochemistry of Substitution via a Trigonal Bipyramid[96].

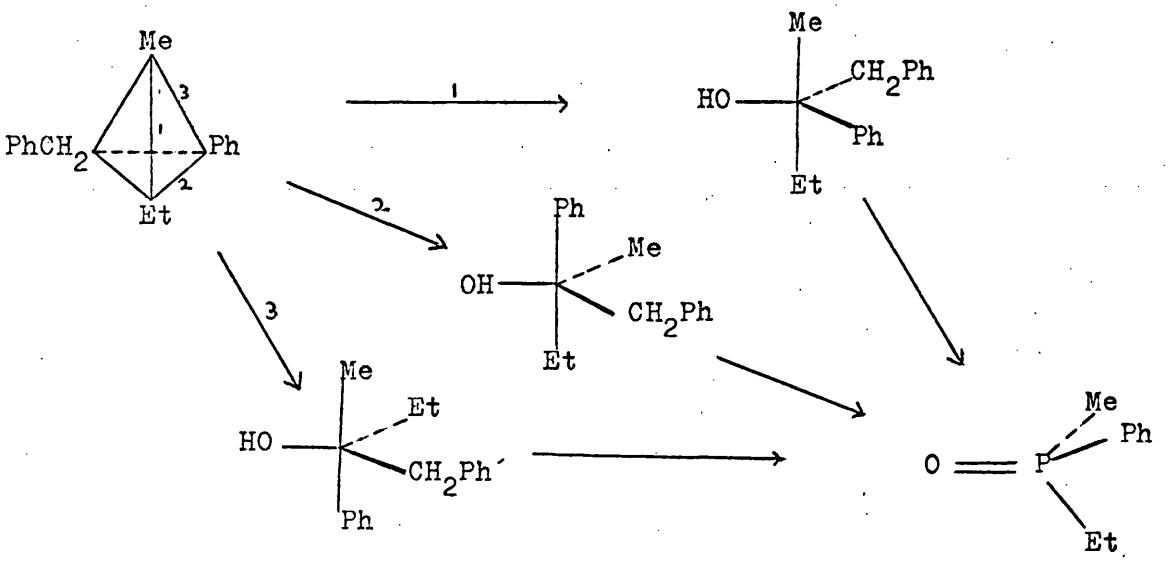
Entry	Exit	Stereochemistry	
a	a	I	
a	e	R	I = inversion
e	a	R	R = retention
e	e	I	

As the hydrolysis of benzylethylmethylphenylphosphonium iodide proceeds with inversion of configuration at phosphorus, the two possible pathways are via either apical attack and apical loss, or equatorial attack and equatorial loss.

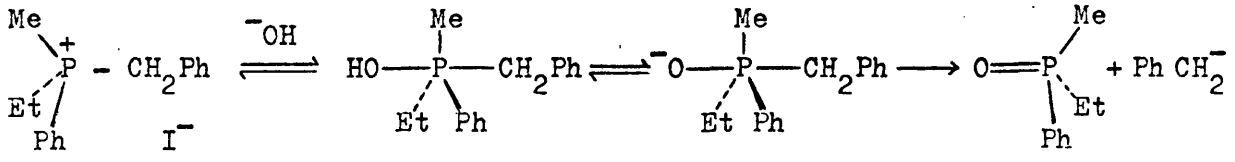
In apical attack, it is possible for the hydroxyl ion to attack all four faces of the tetrahedral phosphonium cation with the result that all four possible pentacoordinate intermediates may be formed. However, as the decomposition of this intermediate is dependent upon the stability of the leaving group as an anion, the benzyl anion will be the only group

lost. As this hydrolysis proceeds with inversion of configuration, the benzyl group must be lost from the other apical position.

Parasitic equilibria may also occur in equatorial attack where attack on all six edges of the tetrahedron could take place. Attack on three of these edges (1, 2, or 3), between any pair of groups which do not include benzyl, would place that benzyl group in an equatorial position such that its loss would lead to inversion of configuration at phosphorus.



Although both these two processes are possible, it has been assumed up till the present that substitutions with inversion of configuration at phosphorus have been proceeding through apical attack - apical loss[88]. Thus the mechanism for the hydrolysis of (+) benzylethylmethylphenylphosphonium iodide has been postulated as follows, assuming that no pseudorotation[103] takes place.



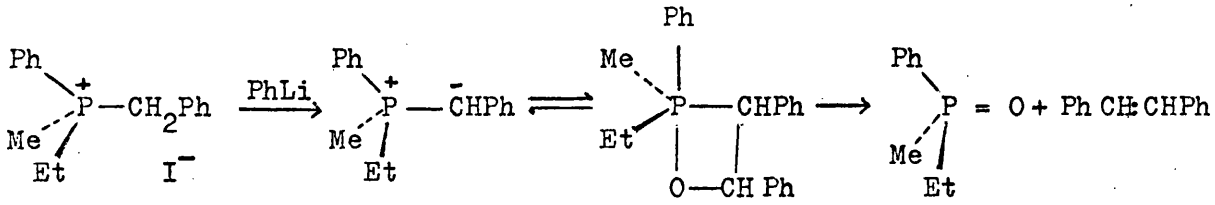
If however there was no good leaving group present in the phosphonium cation, then the rate of decomposition of the intermediate phosphorane would be decreased. The situation might then arise when the rate of pseudorotation[103] would become comparable with the rate of hydrolysis. In such a case an optically active phosphonium salt could hydrolyse with

partial racemisation [104].

In the alkaline hydrolysis of optically active benzylphosphonium salts, the only hydrolyses of optically active phosphonium salts so far reported, the rate of hydrolysis appears to be greater than the rate of pseudorotation, as these reactions are reported to proceed stereospecifically with inversion of configuration[8, 92]. Further evidence for the absence of extensive pseudorotation during nucleophilic substitution reactions at phosphorus has been provided by Hudson and Green[105]. They treated the optically active ^{14}C labelled methyl ester of ethylphenylphosphinic acid with methanol and found that each substitution reaction at phosphorus proceeded with inversion of configuration.

Stereochemistry of the Wittig Reaction.

It has been proposed that a consideration of the mechanism of the Wittig reaction would indicate retention of configuration at phosphorus[94].



(CV) (CVI)

Optically pure dextrorotatory benzylléthylmethylphenylphosphonium iodide (CV), on treatment with phenyllithium followed by benzaldehyde, gave optically pure dextrorotary ethylmethylphenylphosphine oxide[8,91]. Horner and co-workers also found that the oxide from the oxidation of ethylmethylphenylphosphine had the same sign and value of rotation as the phosphine oxide from the Wittig reaction of the benzyl salt prepared by quaternisation of the same enantiomer of the phosphine[91]. As quaternisation[107] and oxidation with hydrogen peroxide[91,92] are believed to proceed with retention of configuration at phosphorus, then the Wittig reaction must also be proceeding with retention of configuration.

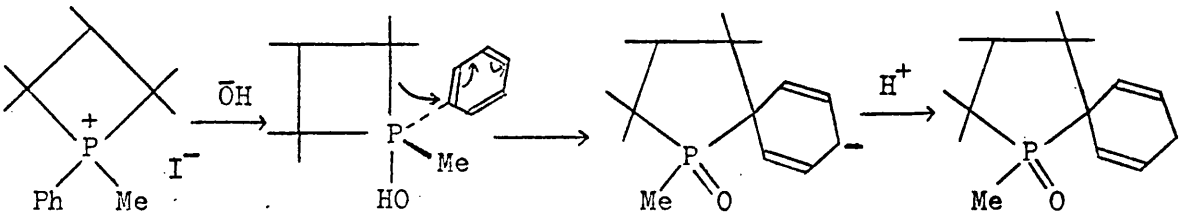
The pentacoordinate intermediate (CVI) which is assumed to be a trigonal bipyramid [97], could alter its geometry sufficiently to bring about inversion of configuration at phosphorus, only by placing the ring diequatorial. Such a process is unlikely to take place.

The Alkaline Hydrolysis of Phosphetanium Salts.

The Pentamethylphosphetanium System.

The alkaline hydrolysis of phosphetanium salts could exhibit anomalous properties if the mechanism for alkaline hydrolysis of acyclic phosphonium salts involved apical attack-apical loss. The four-membered ring would span one apical and one equatorial position in the trigonal bipyramidal intermediate and provided that the apical ring carbon was not the best leaving group in the system, the process of apical attack of hydroxide ion followed by loss of the group most stable as its anion from the other apical position[88] would be thwarted.

This hypothesis was substantiated by Hawes and Trippett [66,67,108], in the initial study in this field. They found that the alkaline hydrolysis of 1,2,2,3,4,4,-hexamethyl-1-phenylphosphetanium iodide (CVII) gave a phosphine oxide whose structure was shown to be the spirophospholane oxide (CVIII) by spectroscopic[67] and deuterium labelling[66] experiments.

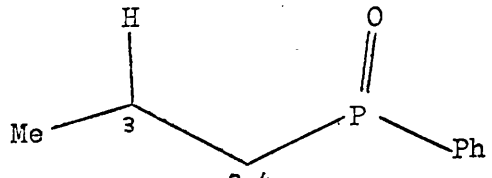


(CVII) (CIX) (CVIII)

In this reaction the apical position of the intermediate was occupied by a very poor leaving group. The most favourable process was the migration of the apical $-CMe_2$ group to the α-carbon of the phenyl ring leading to the formation of a phospholane oxide (CVIII).

By means of a variation [66,68] of the phosphetane synthesis of Jungermann and McBride[65], whereby phosphorus trichloride was replaced by phenylphosphonous dichloride, the two stable geometrical isomers of 2,2,3,4,4-pentamethyl-1-phenylphosphetane-1-oxide were produced and could be separated from one another by chromatography on basic alumina.

Both phosphine oxides were highly crystalline, one having a melting point at 126°C, the other at 118°C. An X-ray crystallographic study on one of the isomers, believed to have m.p. 126°, showed that (a) the four membered ring was puckered, (b) the bond angle of the ring at phosphorus was either 90.8° or 91.1°, and (c) the phenyl group and the methyl group on carbon 3 were cis to oneanother with the C (3)-methyl and P-phenyl bonds almost coplanar (CX) [109].

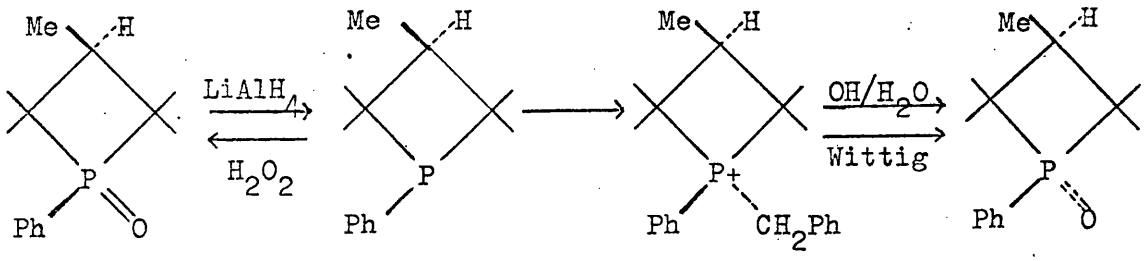


(CX)

Thus the phenyl and C(3)-methyl groups in the other isomer (m.p. 118°C) are trans. The nomenclature used in this discourse will be as follows. The pentamethylphenylphosphetane oxide, m.p. 126°, and all compounds with the same geometry for P-phenyl and C(3)-methyl will be denoted cis. The pentamethylphenylphosphetane oxide, m.p. 118°C, and all compounds with the same geometry will be denoted trans.

By analogy with the hexamethylphenylphosphetanium salt (CVII), the alkaline hydrolysis of 1-benzyl-2,2,3,4,4-pentamethyl-1-phenylphosphetanium bromide (CXI) might also be expected to give a spirophospholane oxide. However, Hawes and Trippett[66,108] found that the products of this reaction were 2,2,3,4,4-pentamethyl-1-phenylphosphetane-1-oxide and toluene.

In order to determine the stereochemistry of this hydrolysis, a number of reactions of known stereochemistry were carried out. Reduction of cis-pentamethyl-1-phenylphosphetane oxide (CX) gave the corresponding phosphetane which on oxidation with hydrogen peroxide gave the cis-phosphetane oxide (CX). Quaternisation of this phosphetane with benzyl bromide produced cis-1-benzyl-2,2,3,4,4-pentamethyl-1-phenylphosphetanium bromide (CXI), which gave the cis-phosphetane oxide (CX) in both alkaline hydrolysis and the Wittig reaction.



(CX) (CXI)

As the Wittig reaction, and oxidation and quaternisation of a phosphine proceed with the retention of configuration and as the cis and trans phosphetane oxides were not interconvertible under the conditions of hydrolysis, so the alkaline hydrolysis of cis-pentamethylphenylphosphetanium bromide (CXI) was proceeding with retention of configuration at phosphorus.

This reaction was the first reported case of a phosphonium salt hydrolysis proceeding with retention of configuration, so it was considered that a study of the stereochemistry of reactions on the trans geometrical isomer would be of interest.

The cis:trans ratio of 2,2,3,4,4-pentamethyl-1-phenylphosphetane-1-oxide could be varied by alterations to the procedure in the later stages of the method of preparation. Pouring the reaction mixture slowly on to ice yielded a cis:trans ratio of 1:4[68]. Chromatography on basic alumina again gave effective separation of these isomers.

Reduction of the pure trans phosphetane oxide was carried out under the mildest conditions possible in order to avoid isomerisation of the phosphetane[69]. However, even when the reduction was carried out with trichlorosilane in methylene chloride at 0°C followed immediately by quaternisation with benzyl bromide at 0°C, at least 10% inversion took place. When the usual conditions necessary for the reduction of an acyclic phosphine oxide were used, i.e., refluxing with trichlorosilane in benzene for 6 - 15 hours[110,111], up to 30% inversion took place. All attempts to obtain a pure sample of trans-1-benzyl-2,2,3,4,4-pentamethyl-1-phenylphosphetanium bromide by fractional crystallisation of the salt and by alteration of the reduc-

tion conditions of the trans phosphetane oxide failed.

The isomerisation of 1-phenyl- and 1-t-butyl-2,2,3,4,4-pentamethylphosphetane has been studied by Cremer and coworkers[69], who found that the energy of activation for this process was about 29k. cals/mole, a value very similar to that obtained by Horner and Winkler[112] for the racemisation of acyclic optically active phosphines.

The reduction of a phosphetane oxide was brought about very readily, as shown by the very mild conditions required. This is believed to be due to the relief of strain in the ring accompanying the process of reduction. As the four membered ring prefers a bond angle of approximately 90° at phosphorus, a phosphine, whose preferred bond angle in an acyclic species is about 100° [9], will be less strained than a phosphine oxide, whose preferred angle is 108°.

Aqueous alkaline hydrolysis of an isomeric mixture of 1-benzyl-2,2,3,4,4-pentamethyl-1-phenylphosphetanium bromide (cis:trans::1:9) gave 2,2,3,4,4-pentamethyl-1-phenylphosphetane-1-oxide having an isomer ratio cis:trans::91:9. Thus as the cis-benzylphosphetanium salt hydrolyses with retention of configuration[108], the hydrolysis of the trans-benzylphosphetanium salt has proceeded with about 90% inversion of configuration and 10% retention of configuration at the phosphorus atom. The isomer ratio of the phosphetane oxide hydrolysis product was found to be independent of the concentration of aqueous sodium hydroxide over the range 0.02N to 5N. Likewise, the alkaline hydrolysis of an isomeric mixture of benzylpentamethylphenylphosphetanium bromide (cis:trans::28:72) gave the corresponding pentamethylphosphetane oxide having an isomer ratio cis:trans::9:1 independent of hydroxyl ion concentration.

It may at first seem surprising that very similar isomer ratios for the phosphetane oxide were obtained from the hydrolysis of two mixtures having different isomeric compositions. However, the phosphetane oxide product isomer ratios were determined by a comparative

^{1}H N.M.R. technique which was accurate to two units either side of the value given (e.g. the maximum deviation for a ratio of 91:9 was 93:7 to 89:11). There was also a greater inaccuracy in the interpolation of results as isomer mixtures were used to investigate the stereochemistry of a reaction, especially when the two isomers followed neither the same nor exactly opposite stereochemical courses.

A partial alkaline hydrolysis of benzylpentamethylphenylphosphetanium bromide with isomer ratios cis:trans::1:9 and 28:72 showed, by ^{1}H N.M.R. analysis, that in both cases the isomer ratio in the unreacted salt was unchanged and that the phosphetane oxide hydrolysis product had the isomer ratio cis:trans::9:1.

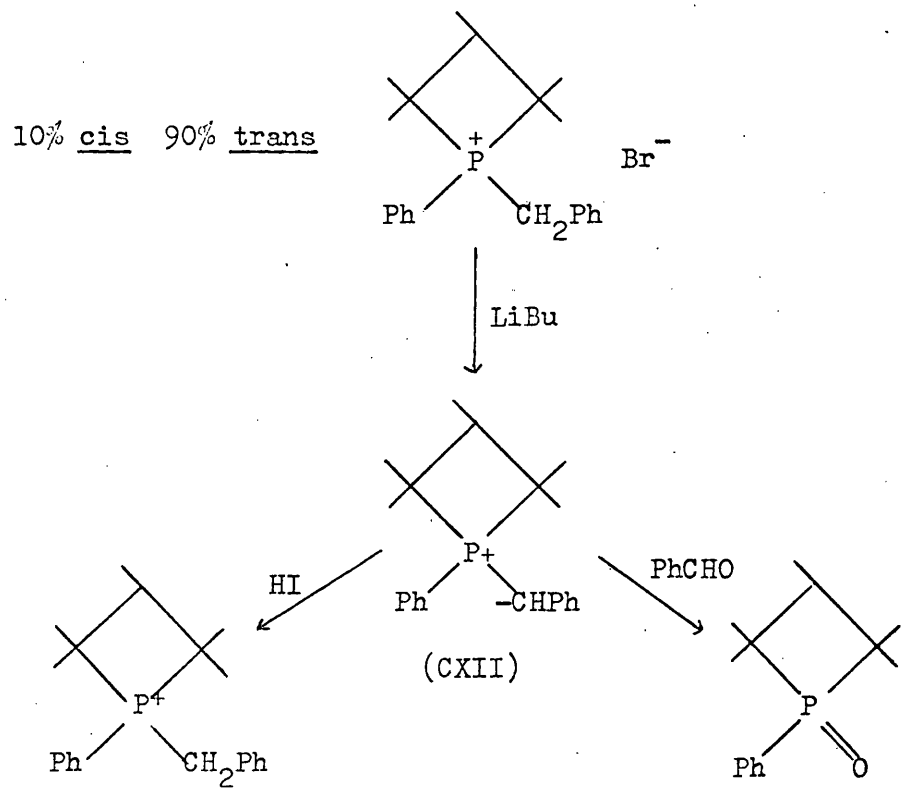
A study of the Wittig olefin synthesis on 1-benzyl-2,2,3,4,4-pentamethyl-1-phenylphosphetanium bromide, having the isomer ratio cis:trans::1:9 also produced an interesting result.

The phosphetanium salt with 1:9 isomer ratio was treated with an equimolar quantity of butyllithium to form the benzylidene ylid. This ylid solution was stirred for ½ hour, when an excess of benzaldehyde was added. ^{1}H N.M.R. analysis of the phosphetane oxide products showed the isomer ratio to be cis:trans::1:1. This result would appear to demonstrate that the Wittig olefin synthesis was not stereospecific! However, the following experiment demonstrated that the Wittig reaction was in fact stereospecific and that isomerisation of the benzylidene ylid was taking place.

The benzylidene ylid of the phosphetanium salt (cis:trans::1:9) was again generated and its solution was stirred for 75 minutes. Half of this ylid solution was added to excess 66% aqueous hydriodic acid whilst the other half was treated with an excess of benzaldehyde. The benzylpentamethylphenylphosphetanium salt from the former reaction was found to have the isomer ratio cis:trans:55:45, whilst the pentamethylphenylphosphetane oxide from the Wittig reaction had the isomer ratio

cis:trans::57:43. When this experiment was repeated with stirring of the ylid solution for 18 hours, the benzylphosphetanium salt had the isomer ratio cis:trans::59:41, whilst the phosphetane oxide had the isomer ratio cis:trans::61:39.

The values for the isomer ratio in the regenerated phosphetanium salt and the phosphetane oxide from the corresponding Wittig reaction are the same within experimental error. Thus inversion of configuration was occurring at the phosphorus atom in the benzylidene ylid (CXII).

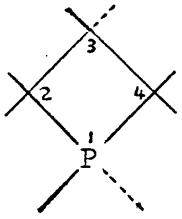


	c : t	c : t
30 min.	--	50 : 50
75 min.	55 : 45	57 : 43
18 hrs.	59 : 41	61 : 39

Mechanism of Isomerisation.

In all investigations into the stereochemical course of reactions at the phosphorus atom in the 2,2,3,4,4-pentamethyl-1-phenylphosphetane system, the method for the detection of stereochemical changes at phosphorus is dependent upon geometrical isomerism across the ring and not upon the absolute stereochemistry at the phosphorus atom.

Thus, any geometrical change observed by the ^{1}H N.M.R. technique used, could in fact be due to changes in the stereochemistry either at phosphorus or at carbon (3) of the ring.



There are three possible processes by which inversion can take place during hydrolysis and in the ylid. Two of these processes deal with direct changes in stereochemistry at phosphorus, the third is a change in stereochemistry at the carbon atom at position 3 in the ring.

Both alkaline hydrolysis and ylid formation require the use of strong base, so it was conceivable that when these two reactions were carried out on the highly strained, highly substituted and puckered 2,2,3,4,4-pentamethylphosphetane system[109,113,114] base would remove the proton from the carbon at position 3.

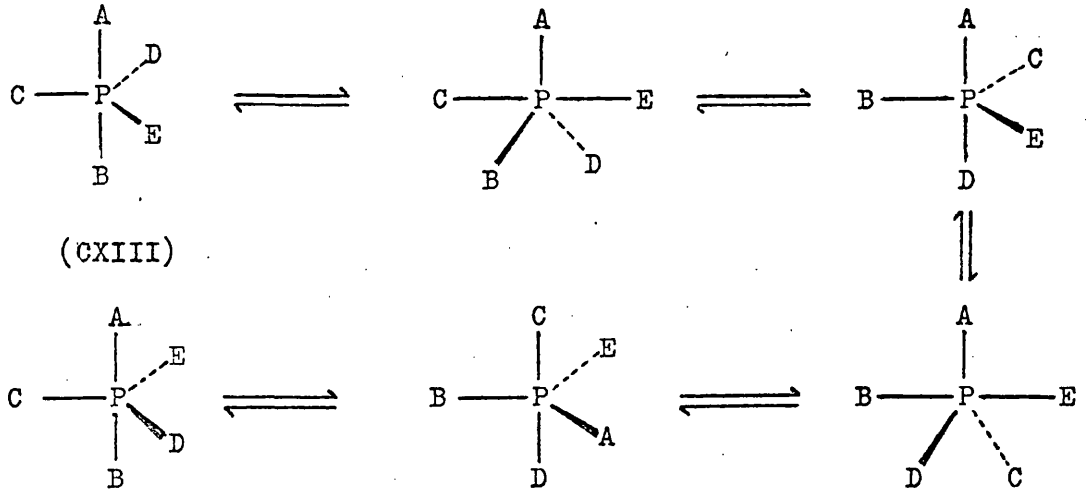
When protonation took place, the more stable isomer would be preferred. Thus cis compounds, presumably the more stable, would proceed with retention of configuration, whereas the trans compounds would proceed with partial inversion of configuration.

Two experimental facts rule out this process. Firstly, the cis and trans isomers of 2,2,3,4,4-pentamethyl-1-phenylphosphetane-1-oxide were not interconvertible in the presence of acid or base[66]. In fact the trans isomer can be treated with refluxing 10N aqueous sodium hydroxide solution for two days without isomerisation or decomposition. Secondly, when the isomer mixture (cis:trans::1:9) of 1-benzyl-2,2,3,4,4-pentamethyl-1-phenylphosphetanium bromide was hydrolysed with excess 0.1N sodium deuteroxide in D_2O, the pentamethylphosphetane oxide with isomer ratio cis:trans::91:9 was isolated in 98% yield. This mixture of oxides showed no incorporation of deuterium at carbon 3 or anywhere else in the molecule.

Thus partial inversion of configuration is occuring at the phosphorus atom itself during alkaline hydrolysis of, and ylid formation from, the trans-benzylpentamethylphenylphosphetanium salt. Two processes are possible for this inversion, pseudorotation and ylid isomerisation.

Pseudorotation.

Pseudorotation is a process of ligand reorganisation such that interconversion between two trigonal bipyramids takes place via a tetragonal pyramidal intermediate. Muetterties has postulated[104] that for a phosphorane containing five different substituents, five pseudorotations, each with a different group as pivot, would cause inversion of configuration about the phosphorus atom as shown below:

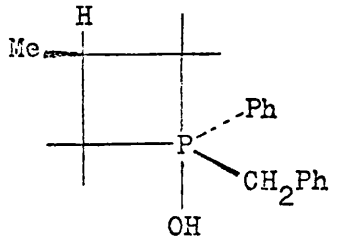


(CXIII)

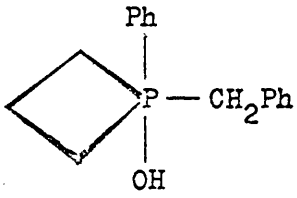
(CXIV)

As can be seen from the diagram, structure (CXIII) is the mirror image of (CXIV).

The initially formed intermediate in the alkaline hydrolysis of 1-benzyl-2,2,3,4,4-pentamethyl-1-phenylphosphetanium bromide would have a trigonal bipyramidal structure with the four membered ring spanning an apical and one equatorial position in a relatively strain free position and with the hydroxyl group in the other apical position as shown in structure (CXV).

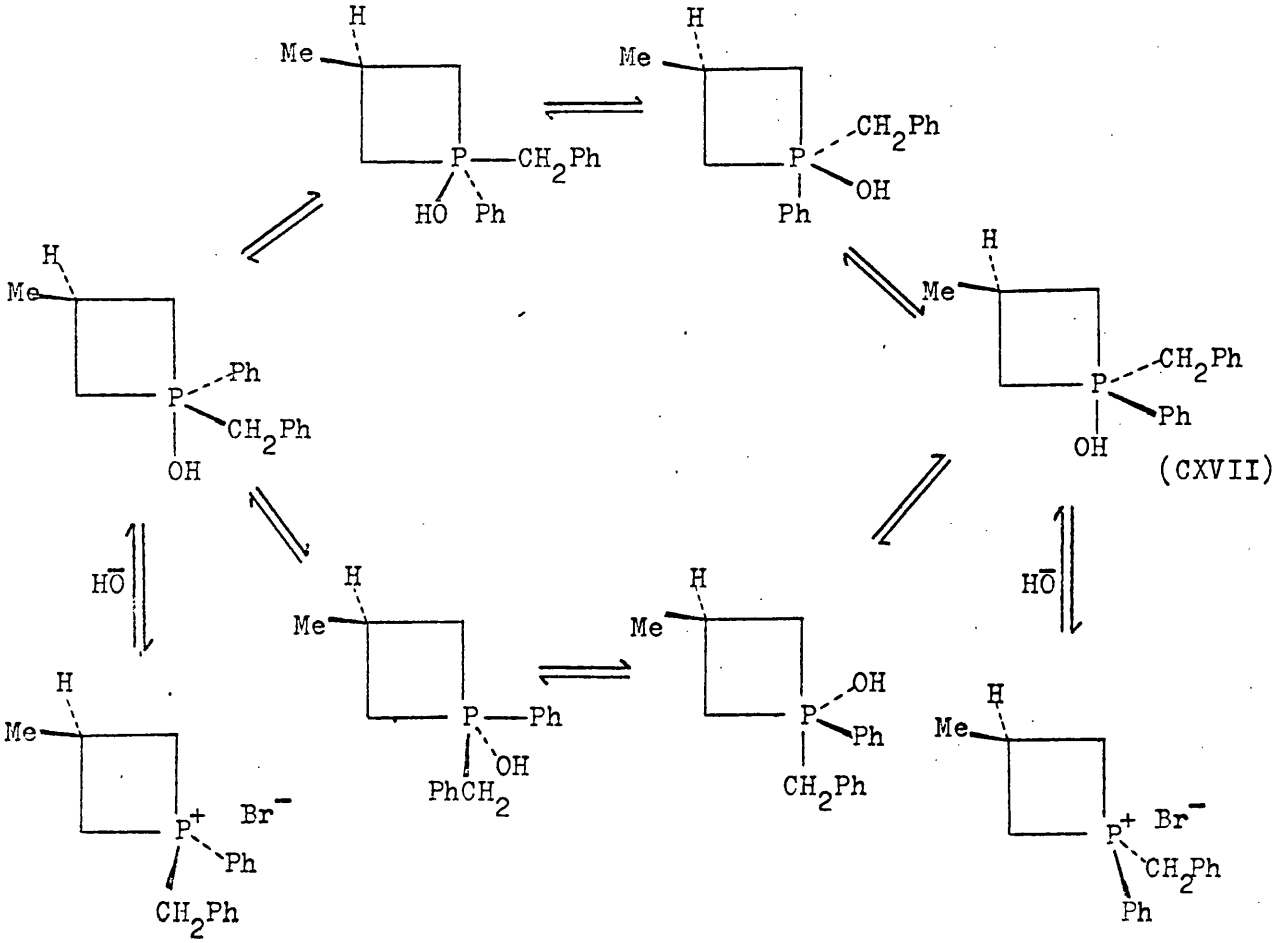


(CXV)



(CXVI)

It would appear that intermediate (CXV) could only invert by placing the ring diequatorial, as shown in (CXVI), a process considered highly unfavourable. However, there is a much simpler process for inversion of configuration by pseudorotation. In this process the ring remains apical-equatorial throughout the three pseudorotations.



(CXVII)

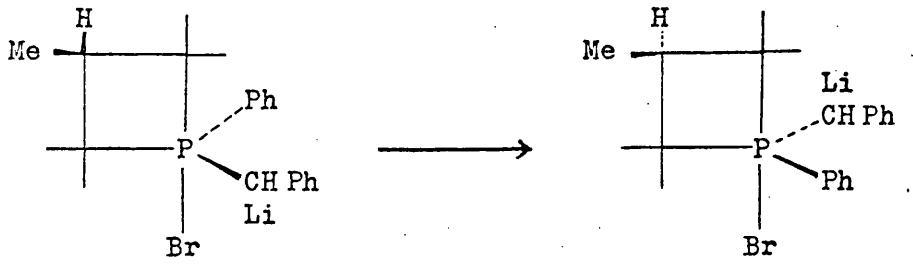
trans cis

Thus, if pseudorotation is the process by which inversion is occurring in the hydrolysis of the trans-benzylphosphetanium salt, the rate of loss of the benzyl group is somewhat slower than the overall rate of at least two, or possibly three pseudorotations

required for inversion of configuration. The pseudorotation process must be extremely fast as the rate of hydrolysis of these salts is very much greater than that of their acyclic analogues.

As pseudorotation processes are believed to be equilibria[104], then it should be possible for the intermediate (CXVII) in the hydrolysis of the cis-phosphetanium salt to pseudorotate according to the above scheme leading to partial inversion of configuration. However, it is known that the cis-phosphetanium salt hydrolyses with retention of configuration[108] so one of the equilibria in the inversion process lies completely on the side of the cis configuration, due possibly to steric, geometric or electronic factors.

This theory, for inversion of configuration in the reactions of trans-benzylphosphetanium salts, fails to explain isomerisation of benzylidene ylids, for the ylid is tetrahedral in structure and so cannot undergo pseudorotation. The only way so far devised for the formation of a pentacoordinate phosphorus atom is to postulate a lithium bromide adduct of the ylid (CXVIII)[6].



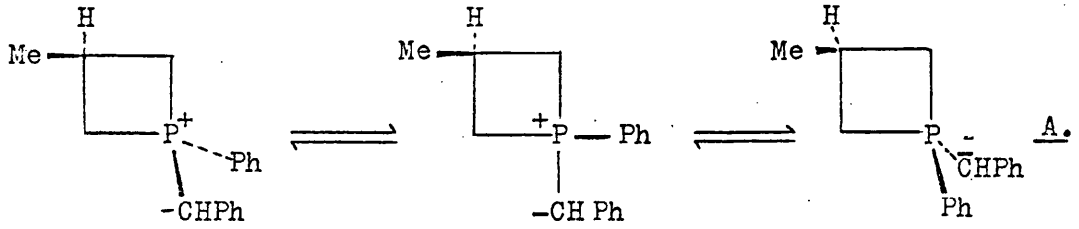
(CXVIII)

This structure (CXVIII) could then pseudorotate in the same manner with similar constraints upon the system as in the alkaline hydrolysis. However, this mechanism cannot be considered as a satisfactory explanation for the inversion of configuration of the trans-benzylidene ylid.

Ylid Isomerisation.

The second mechanism for inversion of configuration is that of ylid isomerisation.

The benzylidene ylid, generated from the benzylphosphetanium salt by treatment with butyllithium, is approximately tetrahedral in structure. Isomerisation of the trans ylid (CXIX) to the cis ylid (CXX) is postulated as proceeding through a square planar configuration (CXXI).



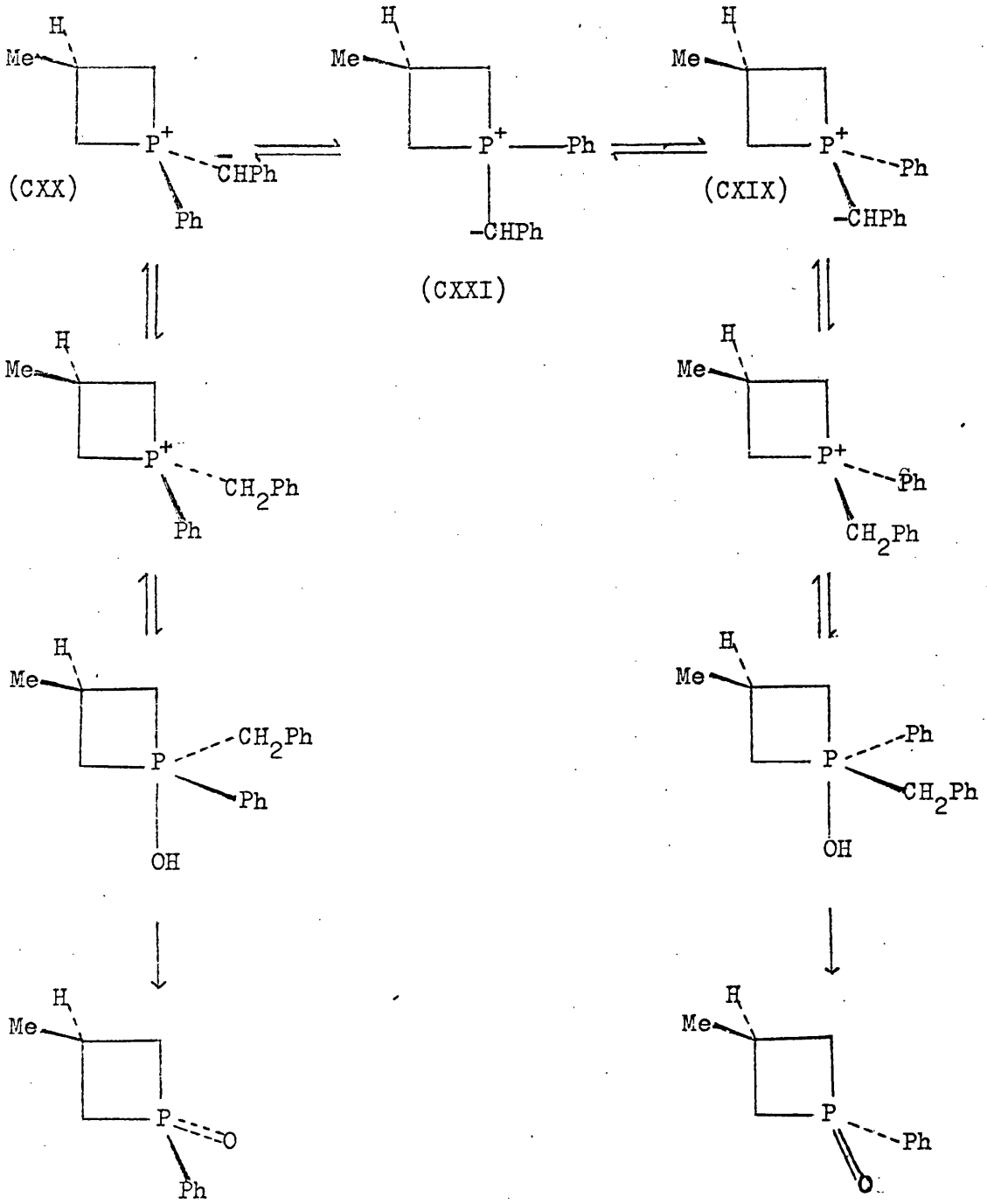
(CXIX) (CXXI) (CXX)

Equation A is in fact an idealised representation, for the nature of structure (CXXI) is not known. Also the process of isomerisation is not in fact a true equilibrium, for although the trans ylid (CXIX) can isomerise to the cis ylid (CXX), the reverse process does not occur, probably due to the greater stability of the cis configuration.

This process of ylid isomerisation is also postulated for the alkaline hydrolysis of the trans benzyl salt. A benzylic proton of a benzylphosphetanium salt is readily removed in basic medium and a series of equilibria are set up between the cis and trans phosphetanium salts and their respective ylids, as shown in the diagram on the following page.

The cis phosphetanium salt hydrolyses with retention of configuration so that the rate of inversion of the ylid (CXX) must be much slower than the rate of hydrolysis. In the trans phosphetanium salt, however, hydrolysis occurs at a similar or slightly slower rate, than yild inversion, so the overall hydrolysis proceeds with partial inversion of configuration.

CIS SERIES TRANS SERIES

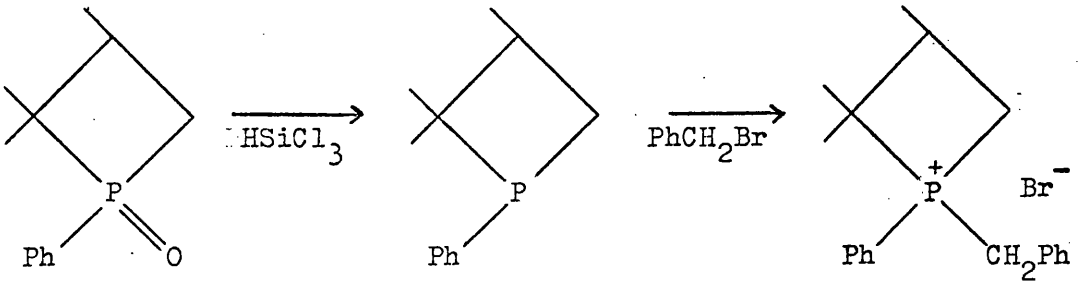


Conclusion

Neither mechanism offers a completely satisfactory explanation on the evidence available, though at present the ylid isomerisation is favoured as one mechanism applies to both reactions. Subsequent investigations may, however, show that pseudorotation is operating in the alkaline hydrolysis, whereas ylid isomerisation occurs in the Wittig reaction.

The Trimethylphosphetane System.

A mixture of the two geometrical isomers of 2,2,3-trimethyl-1-phenylphosphetane-1-oxide (CXXII) was prepared by the reaction of phenylphosphonous dichloride with t-butylethylene [66,68]. These two isomers, present in 19:1 ratio, could be separated neither by fractional crystallisation nor by chromatography on basic alumina. This mixture of oxides could be readily reduced, the isomer ratio of the resulting phosphetane being dependent upon the nature of the reducing medium[68]. Cremer found[68] that the ratio could be varied from 19:1, when an excess of equivalent quantities of pyridine and trichlorosilane was used, to 1:1, when equimolar quantities of triethylamine and trichlorosilane were used [115].



(CXXII)

Quaternisation of the phosphetane isomer mixtures with benzyl bromide gave the corresponding isomer mixture of 1-benzyl-2,2,3-trimethyl-1-phenylphosphetanium bromide. The two geometrical isomers of this benzylphosphetanium salt could not be effectively separated by fractional crystallisation. However, it was possible to bring about an increase in concentration of one of the isomers by this process. Thus the final residue from the fractional crystallisation of 23g. of the benzyltrimethylphosphetanium salt with a 1:1 isomer ratio consisted of ½g. of an isomer mixture with the approximate ratio 1:3.

The accurate estimation of isomer ratios in the trimethylphosphetane system proved very difficult. Firstly, no pure samples of the two oxides or benzyl salts could be obtained, consequently no

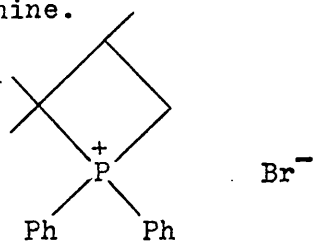
standard mixtures for ^{1}H N.M.R. analysis could be prepared. Secondly, estimation of the ratios by proton N.M.R. integration techniques was inaccurate because of overlap of the peaks of the two isomers. The only satisfactory solvent for the trimethylphosphetane oxide proved to be benzene, whereas no satisfactory solvent could be found for the benzyl salt. Usually deuteriochloroform was a satisfactory solvent for benzylphosphetanium salts as the doublet due to the benzyl group of one geometrical isomer was well separated from that due to the other isomer. However, 1-benzyl-2,2,3-trimethyl-1-phenylphosphetanium bromide (19:1 isomer ratio) in this solvent exhibited four peaks whose intensities were temperature dependent. In trifluoracetic acid, the same phosphetanium salt mixture exhibited a doublet in the ^{1}H N.M.R., but as with the benzylpentamethylphosphetanium salts in the same solvent, there was effective overlap of the signals from the two isomers. Estimation of isomer ratios from the alkyl region of the spectrum proved to be only slightly more successful.

The alkaline hydrolysis of 1-benzyl-2,3,3-trimethyl-1-phenylphosphetanium bromide was found to exhibit properties analogous to the benzylpentamethylphosphetanium salt. It was found that one isomer, that usually in excess, underwent both the Wittig reaction and alkaline hydrolysis with retention of configuration at phosphorus. The other isomer underwent both reactions with partial inversion of configuration. The alkaline hydrolysis of this isomer proceeded with approximately 60% inversion and 40% retention of configuration at the phosphorus atom. The two geometrical isomers of 2,2,3-trimethyl-1-phenylphosphetane-1-oxide were not interconvertible under the conditions of hydrolysis.

Synthesis of 2,2,3-Trimethyl-1,1-diphenylphosphetanium Bromide.

Several attempts were made to synthesise 2,2,3-trimethyl-1,1-diphenylphosphetanium bromide, but all were completely without success. Three

attempts to quaternise trimethylphenylphosphetane were by Horner's complex salt method[24] using bromobenzene and nickel bromide in benzonitrile, by Horner's diazonium salt method[116], and a variation on the latter using benzene diazonium fluorborate in ethyl acetate[117]. The fourth attempt was a variation on the phosphetane synthesis of Jungermann and McBride[65], where phosphorus trichloride was replaced by diphenylchlorophosphine.



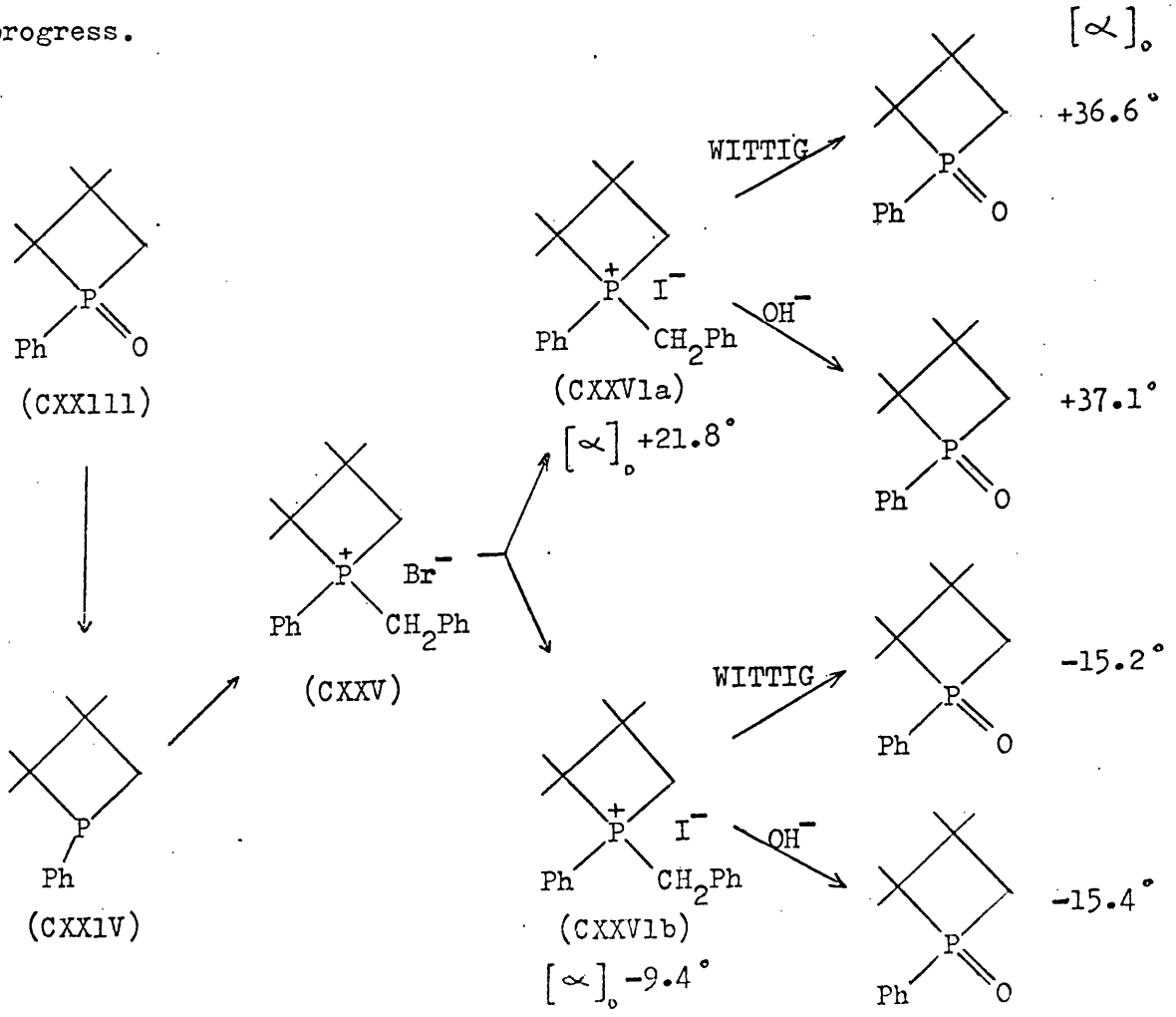
The Tetramethylphosphetane System.

In order to determine the stereochemical changes taking place at phosphorus more directly, a phosphetanium salt with a chiral phosphorus atom but no geometrical isomerism was prepared.

2,2,3,3-Tetramethyl-1-phenylphosphetane-1-oxide (CXXIII) was prepared from 2,2,3-trimethylbut-1-ene and phenylphosphonous dichloride according to Cremer's variation[68] on the synthesis of Jungermann and McBride[65]. This oxide was readily reduced by trichlorosilane-triethylamine[68,110,115] to the phosphetane (CXXIV), which on quaternisation with benzyl bromide gave 1-benzyl-2,2,3,3-tetramethyl-1-phenylphosphetanium bromide (CXXV). The phosphetanium cation of (CXXV) was separated into its optical enantiomers by means of a fractional crystallisation of its D(-)dibenzoyl hydrogentartrate salt from n-propanol[118,119] followed by metathesis with ammonium iodide. This yielded an optically pure dextrorotatory salt (CXXVIa) and an optically impure laevorotatory salt (CXXVIb).

Alkaline hydrolysis of the optically pure dextrorotatory salt (CXXVIa), $[\alpha]_D$ = + 21.8 ± 1° (methanol), with 0.1N sodium hydroxide solution gave 2,2,3,3-tetramethyl-1-phenylphosphetane-1-oxide having $[\alpha]_D$ = + 37.1 ± 1° (methanol). The value for the optical rotation of this phosphetane oxide could not be altered by recrystallisation. Two Wittig reactions, using butyllithium and benzaldehyde, carried out on the same dextrorotatory salt (CXXVIa) gave the corresponding phosphetane oxide with rotations of $[\alpha]_D$ = + 35.0 ± 0.8° and $[\alpha]_D$ = 36.6° ± 0.6° (methanol).

When alkaline hydrolysis and the Wittig reaction were performed on the optically impure laevorotatory benzylphosphetanium salt (CXXVIb), $[\alpha]_D$ = -9.4° ± 1.0° (methanol), the corresponding phosphetane oxide exhibited rotations of $[\alpha]_D$ = -15.4 ± 1° and - 15.2° ± 1° (methanol) respectively. Repeated fractional recrystallisation of this optically impure oxide succeeded in increasing the optical rotation to $[\alpha]_D$ = -29° (methanol), when lack of material hindered further progress.



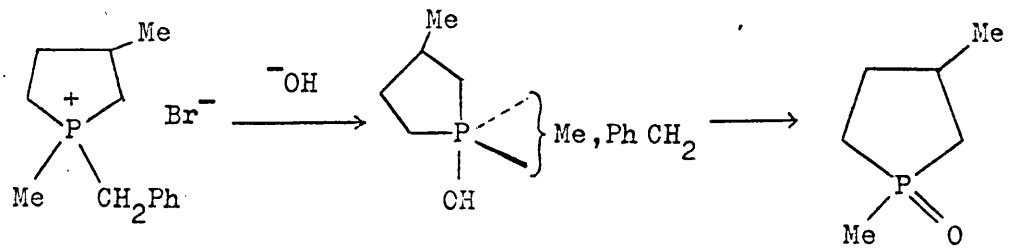
The dextrorotatory oxide from the alkaline hydrolysis exhibited the same O.R.D. curve over the range 589 - 365nm. as the oxide from the Wittig reaction. In fact this curve was very similar in shape to that of methylphenylpropylphosphine oxide as reported by Horner[91].

The rotation of the oxide from the hydrolysis of the deutro-rotatory salt (CXXVIa) could not be altered by recrystallisation, so that oxide was assumed to be optically pure. As the phosphetane oxide from the Wittig reaction on the same enantiomer (CXXVIa) had the same sign and value for the optical rotation, then the alkaline hydrolysis of 1-benzyl-2,2,3,3-tetramethyl-1-phenylphosphetanium iodide was proceeding with 100% retention of configuration at the phosphorus atom.

This experiment demonstrates that ylid interconversion or pseudo-rotation was not occurring in the hydrolysis of the tetramethylphos-phetanium salt (CXXV). Thus it would appear that the partial inversion of configuration occurring in the tri- and penta-methylphosphetanium salts was due to the differing stabilities of the intermediates formed from the two geometrical isomers of each benzyl salt; i.e., the partial inversion process is a phenomenon connected with cis and trans geomet-rical isomerism across the phosphetane ring.

Comparison with Other Systems.

Marsi, in a recent communication[120], reported a second example of retention of configuration in the alkaline hydrolysis of a phosphonium salt. He found that both the cis and trans isomers of 1-benzyl-1,3-dimethylphospholanium bromide (CXXVII) hydrolysed with complete retention of configuration at phosphorus. Consequently neither pseudorotation nor ylid isomerisation could be taking place.



(CXXVII) (CXXVIII)

The phospholane ring is similar to the phosphetane ring in its stereochemical requirement, in that during the hydrolysis of the phospholanium salt, the ring will span one apical and one equatorial position of the trigonal bipyramidal intermediate (CXXVIII). The subsequent loss of a benzyl group would lead to retention of configuration.

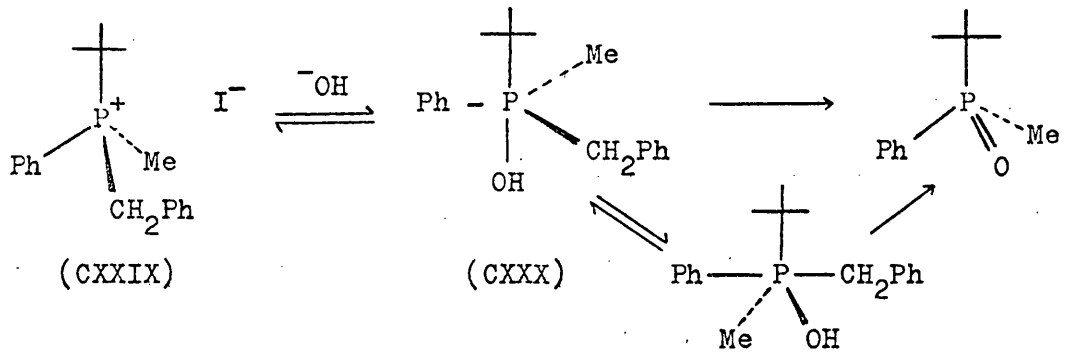
The difference in the stereochemical course of hydrolysis between the trans-benzylpentamethylphosphetanium salt and trans-benzylmethylphospholanium salt can be explained by the greater influence exerted by the methyl group at carbon (3) upon the geometry of the ring in the phosphetane as compared with the phospholane. As a consequence of this, the difference in energy between the hydrolysis intermediates of the cis- and trans-benzylpentamethylphosphetanium salts is much greater than between the hydrolysis intermediates of the cis and trans-phospholanium salts. Thus in trans-benzylpentamethylphosphetanium salts, partial inversion takes place, whereas the trans-phospholanium salt hydrolyses with retention of configuration at phosphorus.

The Positions of Entry and Exit of Groups in the Hydrolysis of Phosphetanium Salts.

This work on the hydrolysis of benzylphosphetanium salts indicates that the hydrolysis of an acyclic benzylphosphonium salt proceeds via apical attack of hydroxyl ion followed by loss of benzyl from the other apical position, for if hydrolysis is proceeding via equatorial attack - equatorial loss, the benzyl-phosphetanium and -phospholanium salts would hydrolyse with inversion of configuration.

For the hydrolysis of a benzylphosphonium salt to proceed with retention of configuration, either apical attack of hydroxyl ion followed by loss of benzyl from an equatorial position, or vice versa, must occur. Of these two possibilities, the former is more favoured, as an acyclic phosphonium salt is also believed to undergo apical attack by the hydroxyl ion.

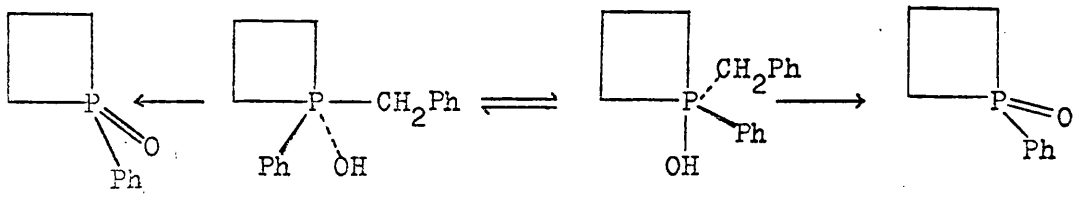
Further support for apical attack of hydroxyl can be drawn from the work of Trippett and De'Ath[121], who found that an optically active t-butylphosphonium salt (CXXIX) hydrolysed largely (79%) with retention of configuration at phosphorus. They proposed that because of the great steric bulk of the t-butyl group, the normal process of inversion of configuration was hindered. Instead, the hydrolysis was proceeding largely (79%) by apical attack of an hydroxyl ion on the face opposite the t-butyl group, giving the intermediate (CXXX).



(CXXIX) (CXXX)

Loss of benzyl from an equatorial position of (CXXX) or pseudorotation of intermediate (CXXX) to place the benzyl group apical, followed by its loss from that position would lead to retention of configuration. Which of these two processes is occurring is not definitely known. In this example, pseudorotation may be inhibited by the requirement of placing a t-butyl group equatorial. However, in an equatorial position there are only two groups perpendicular to it whereas an apical position has three. This may be counterbalanced by the greater length of the apical bond[122].

This situation also occurs in the hydrolysis of benzylphosphetanium salts. In the initially formed intermediate, one apical position is occupied by the hydroxyl group, whilst the ring spans the other apical and one equatorial position. Loss of benzyl could occur either from an equatorial position, or pseudorotation of the intermediate, followed by loss of benzyl from an apical position.



In such a pseudorotation, the electronegative hydroxyl group is moving from an apical to an equatorial position, an unfavourable process according to Muetterties and Westheimer[123]. Also if one pseudorotation were occurring it ought to be possible for several to occur bringing about partial inversion of configuration. For these reasons, the loss of a benzyl group from an equatorial position is at present favoured.

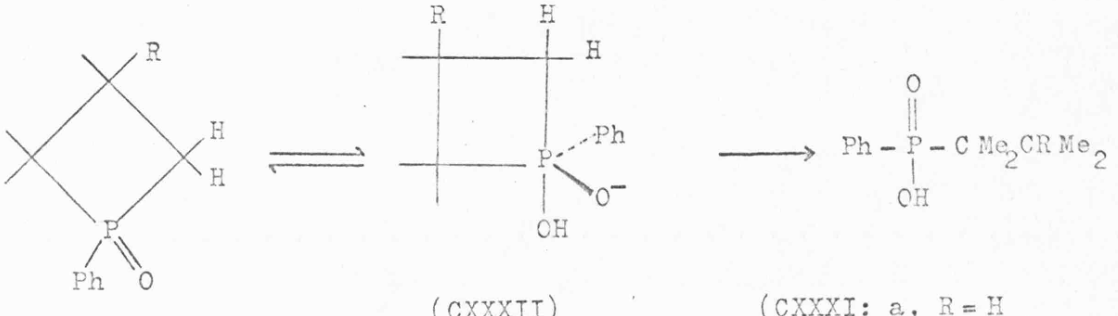
Ring Expansion and Ring Opening Reactions.

(a) Reactions with Sodium Hydroxide.

The alkaline hydrolyses of four and five membered cyclic phosphonium salts and phosphinate esters have been found to proceed very much faster than their acyclic analogues[58,124-126]. This rate enhancement has been attributed to the relief of strain in the four or five membered ring on forming the trigonal bipyramidal intermediate[58,124-8].

The alkaline hydrolyses of 1-benzyl-tri-, tetra- and penta-methylphosphetanium salts carried out in this work were found, on a qualitative basis, to be much faster than the hydrolyses of acyclic benzylphosphonium salts. For example, the hydrolyses of these phosphetanium salts required only 0.1N aqueous sodium hydroxide solution at room temperature for 15 minutes, conditions too mild for the hydrolysis of benzyltriphenylphosphonium bromide.

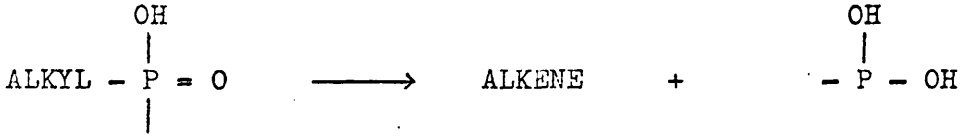
In the tri- and tetra-methylphosphetanium series, this ease of hydrolysis was very fortuitous, for stronger alkaline conditions brought about ring opening of the phosphetane oxide. Refluxing 2,2,3-trimethyl-1-phenylphosphetane-1-oxide with 2N sodium hydroxide - 25% ethanol solution for 72 hours yielded (1,1,2-trimethylpropyl)phenylphosphinic acid (CXXXIa) in very high yield. Likewise 2,2,3,3-tetramethyl-1-phenylphosphetane-1-oxide under similar conditions gave (1,1,2,2-tetramethylpropyl)phenylphosphinic acid (CXXXIb) in 44% yield.



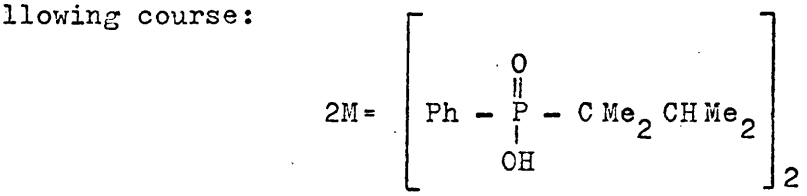
(CXXXII) (CXXXI: a, R = H
b, R = Me)

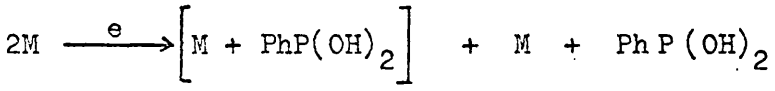
The phosphoryl bond in a phosphine oxide could be considered as existing in the polarised form $\overset{+}{P} - \overline{O}$. In strongly alkaline solution reversible attack of hydroxyl ion at the positive phosphorus would occur, giving the intermediate (CXXXII) in which the ring held a relatively strain-free configuration. This intermediate could break down with ring opening to give the phosphinic acid (CXXXIa, b). Ring opening occurred with loss of $-\overline{C}H_2$ and not $-\overline{C}Me_2$, as the former carbanion was relatively more stable.

The structures of the phosphinic acids were confirmed by physical techniques and analysis. Mass spectral structure determinations showed that both acids appeared as dimeric species, a phenomenon already reported for cyclic phosphinic acids by Dimroth[129]. The breakdown pattern was similar to that reported by Haake[130] for dialkylphosphinic acids.



The phosphinic acids from the ring opening reaction followed the following course:

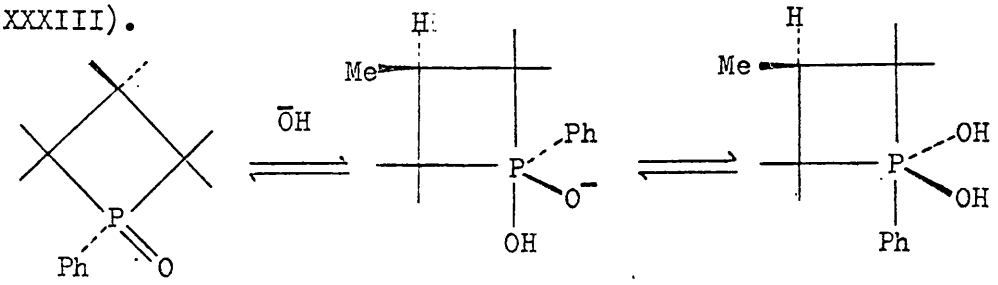




The methyl ester of (1,1,2-trimethylpropyl)phenylphosphinic acid, prepared by treatment of the acid with diazomethane, was monomeric in the mass spectrum.

In contrast to the ring opening of the tri- and tetra-methylphosphetane oxides, the pentamethylphosphetane oxide was completely stable, even in 10N sodium hydroxide solution. This was because the tertiary carbanion $-\overline{C}Me_2$ was not very readily formed. However, as an hydroxyl ion attacks the phosphorus atom of the tri- and tetra-methylphosphetane

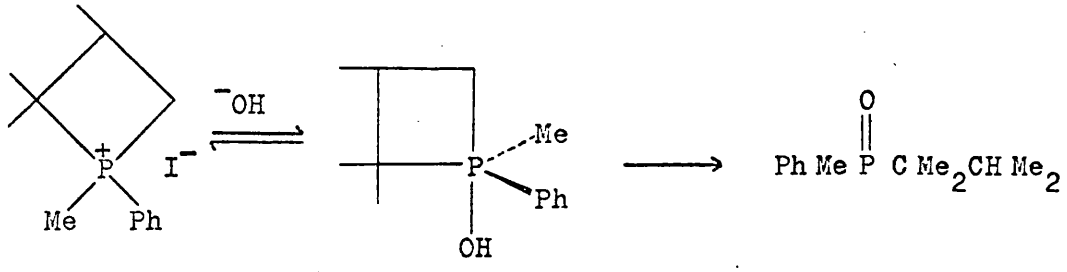
oxides and of the phosphinate ester of the pentamethylphosphetane[124], there seems to be no reason why attack at the phosphorus of the pentamethylphosphetane oxide should not occur, giving the intermediate (CXXXIII).



(CXXXIII) (CXXXIV)

Protonation and pseudorotation of species (CXXXIII) would give (CXXXIV). Loss of an hydroxyl from this structure (CXXXIV) would give a mixture of the two geometrical isomers of the pentamethylphosphetane oxide. As interconversion of the two isomers does not take place, it would appear that pseudorotation of intermediate (CXXXIII) does not occur, possibly because this requires both electronegative hydroxyl groups to be diequatorial in species (CXXXIV).

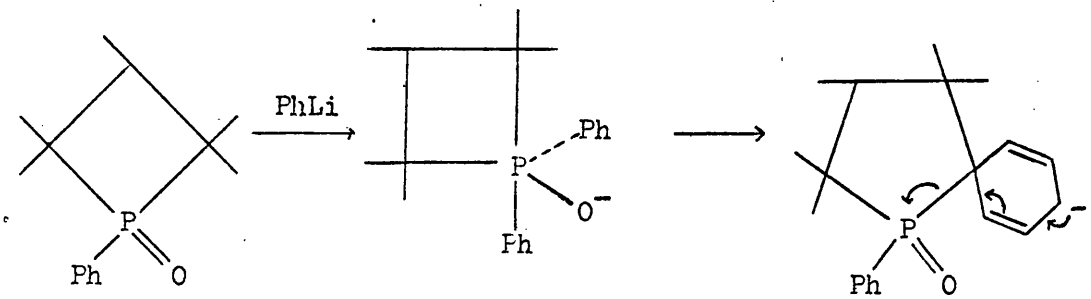
A ring opening reaction in the alkaline hydrolysis of 1,2,2,3-tetramethyl-1-phenylphosphetanium iodide has been reported by Fishwick and Flint[131], who found that the primary and not the tertiary carbanion was produced in ring opening.



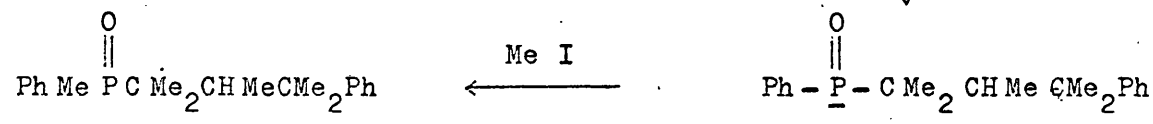
In contrast to this, the analagous salt in the pentamethyl series underwent hydrolysis with ring expansion by migration of $-CMe_2$ from phosphorus to the α-carbon of the equatorial phenyl ring[67] as outlined in the opening section of this discussion.

b) Reaction with Phenyllithium.

Hawes and Trippett found[66] that the reaction of phenyllithium with 2,2,3,4,4-pentamethyl-1-phenylphosphetane-1-oxide resembled mechanistically the alkaline hydrolysis of 1,2,2,3,4,4-hexamethyl-1-phenylphosphetanium iodide[67]. Attack of phenyllithium on the phosphetane oxide gave the pentacoordinate intermediate (CXXXV)



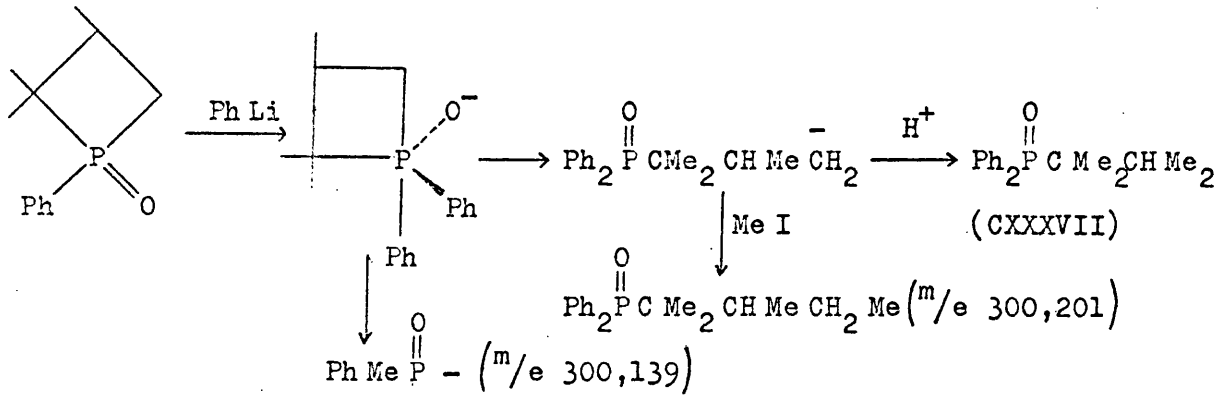
(CXXXV) (CXXXVI)



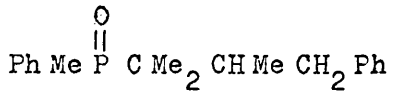
Ring expansion to the ∝-carbon of the equatorial phenyl ring gave the carbanion (CXXXVI) which, in the absence of a proton source, rearranged to the phosphinyl anion. Deuterium labelling studies showed that equilibration of the phenyl groups was taking place in the pentacoordinate intermediate.

In order to determine if an analogous reaction to the hydrolysis of 1,2,2,3-tetramethyl-1-phenylphosphetanium iodide existed, 2,2,3-trimethyl-1-phenylphosphetane-1-oxide was treated with an equivalent quantity of phenyllithium followed by an excess of methyl iodide. Only one pure product could be isolated, namely (1,1,2-trimethylpropyl)-diphenylphosphine oxide (CXXXVII) which was produced by ring opening and protonation of the $-\bar{C}H_2$ carbanion. An oil was also isolated, which was found to contain at least two phosphine oxides. The mass spectrum of this oil showed a mass peak at $^m/e$ 300, i.e., 14 units more than for oxide (CXXXVII), and showed the presence of Ph_2PO ($^m/e$ 201) and Ph Me P O ($^m/e$ 139).

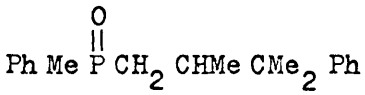
The mechanism for this reaction was visualised as follows:



There are several possible structures for a phosphine oxide showing $^{m}/e$ 300 and 139., but the presence of the Ph Me PO group would indicate that a process directly analogous to that in the pentamethyl-phosphetane series had occurred. Thus the two oxides (CXXXVIII) and (CXXXIX) would be formed by migration of either $-CH_2$ or CMe_2 to the α-carbon of the phenyl ring followed by collapse of the spirophospholane carbanion.



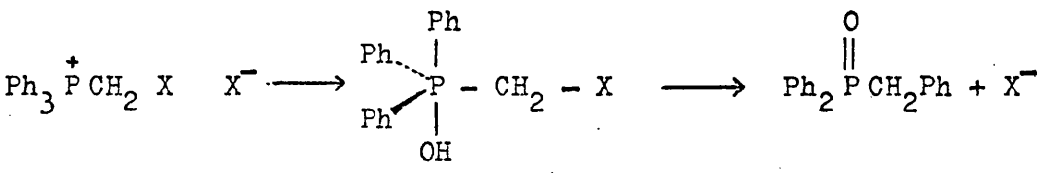
(CXXXVIII)



(CXXXIX)

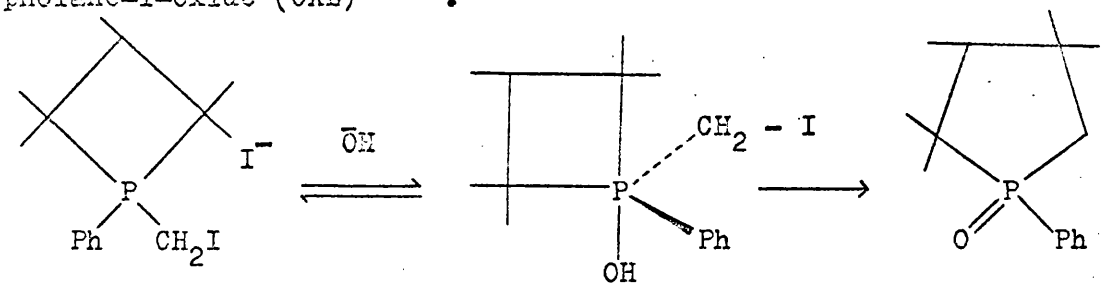
c) Hydrolysis of Iodomethyl Salts.

The alkaline hydrolyses of halomethyltriphenylphosphonium salts have been found to proceed with phenyl migration from phosphorus to the carbon of the halomethyl group with the corresponding loss of halide ion[132,133]. The ease of migration of the phenyl group was dependent upon the ease of loss of halide as an anion; $I^- > Br^- > Cl^-$.



With the knowledge that ring expansion occurred in the alkaline hydrolysis of the hexamethylphosphetanium salt (CVII), Hawes and Trippett subjected the iodomethyl salt of pentamethyl-1-phenylphosphetane to alkaline hydrolysis and obtained 2,2,3,4,4,pentamethyl-1-phenylphos-

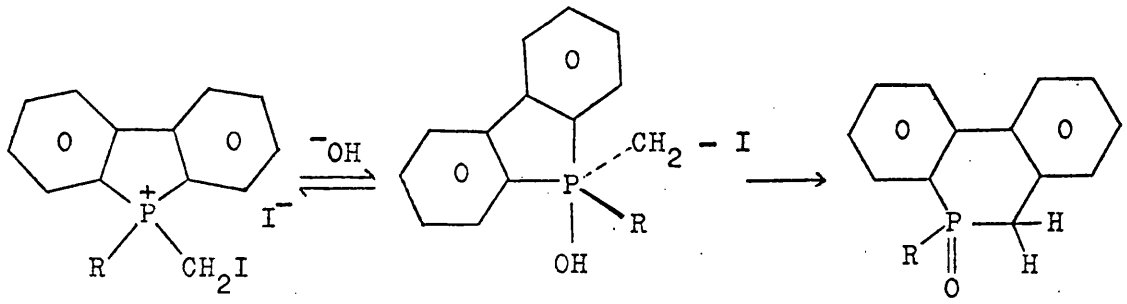
pholane-1-oxide (CXL)[66,67].



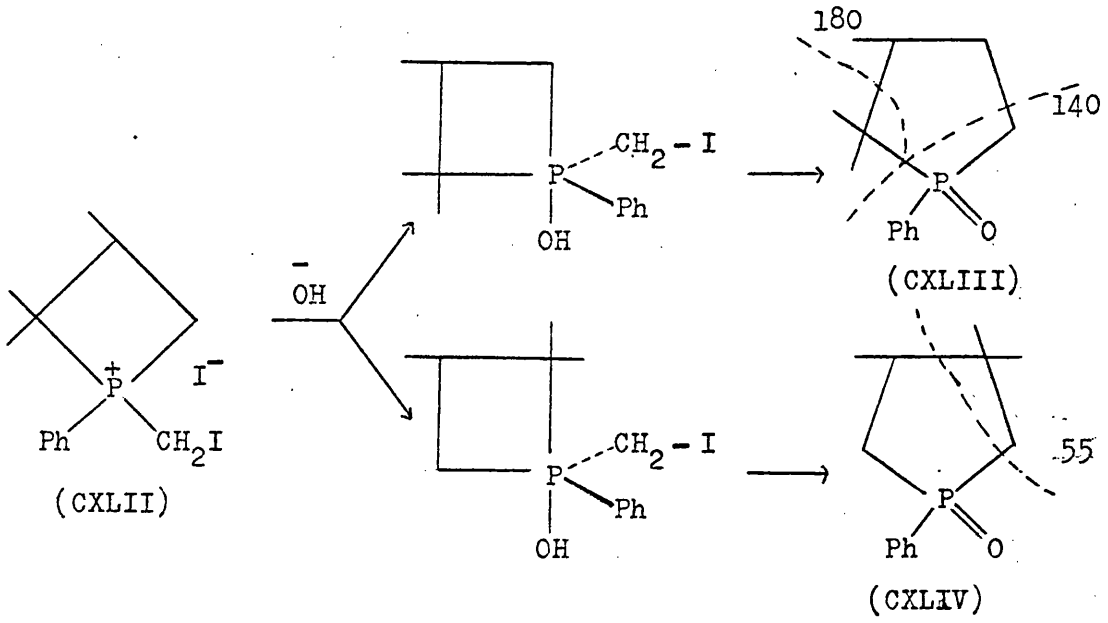
(CXLI) (CXL)

The group which migrates in this hydrolysis does so from an apical position of the trigonal bipyramidal intermediate (CXLI). As the four membered ring prefers to lie apical-equatorial in this intermediate, then migration of $-CMe_2$ rather than the equatorial phenyl group occurs.

More recently, Allen and Millar have reported that the hydrolysis of the methylene iodide salt of a 9-substituted-9-phosphafluorene also proceeded with ring expansion[134,135], as the five membered ring lies apical-equatorial in the intermediate.



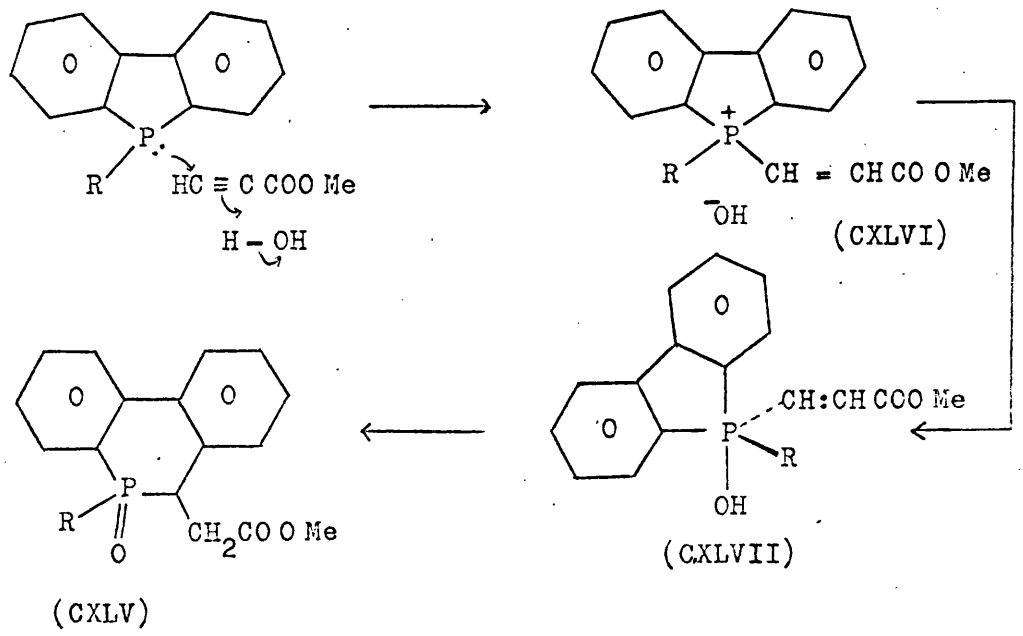
As a consequence of these results, a similar experiment was carried out in the trimethylphosphetane series. Quaternisation of 2,2,3-trimethyl-1-phenylphosphetane (19:1 ratio of isomers) with methylene iodide gave the highly insoluble iodomethyl salt (CXLII). Alkaline hydrolysis of this salt gave a liquid phosphine oxide which was believed to contain the four isomeric phospholanes:- the two geometrical isomers of (CXLIII) and (CXLIV).



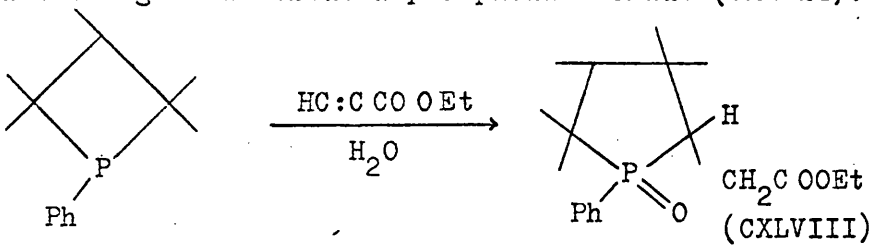
The mixture could not be separated into its components, but the mass spectral breakdown pattern indicated the presence of both structures.

d) Reaction of a Phosphetane with Ethyl Propiolate.

Richards and Tebby found that methyl propiolate reacted with 9-substituted-9-phosphafluorenes in wet ether to give a phospha-phenanthrene (CXLV)[136]. This reaction could be explained by the following mechanism. The phosphine attacked the triple bond of the acetylene to give a phosphonium hydroxide (CXLVI), which in turn gave the hydrolysis intermediate (CXLVII) with the five membered ring once again lying apical-equatorial. This intermediate broke down with migration to the α-carbon of the equatorial vinyl group leading to the ring expanded product (CXLV).

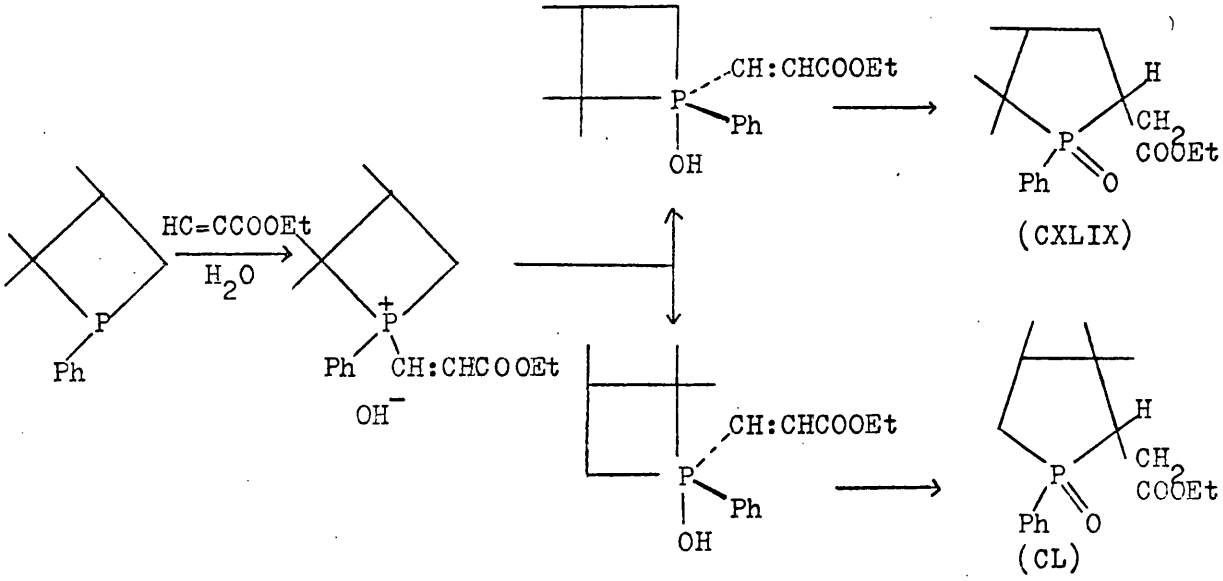


Hawes found[66] that an identical ring expansion took place when cis-pentamethyl-1-phenylphosphetane was treated with ethyl propiolate, the product being a substituted phospholane oxide (CXLVIII).



(CXLVIII)

In order to test the general applicability of this reaction, 2,2,3-trimethyl-1-phenylphosphetane (19:1 isomer ratio) was treated with ethyl propiolate in wet ether. After an exothermic reaction, the products were separated by chromatography on silica. Two liquid phosphine oxides were isolated and were shown by ^{1}H N.M.R., mass spectral and analytical data to be the two possible isomeric phospholane oxides produced by the ring expansion process outlined above.



The liquid nature of the two phospholane oxides (CXLIX) and (CL) was believed to be due to the presence of the two geometrical isomers of each structure. No separation of the individual geometrical isomers could be attained.

Conclusion.

Certain contrasts and similarities can be observed in the reactions described or referred to in this section.

The one property appertaining to all these reactions is that the

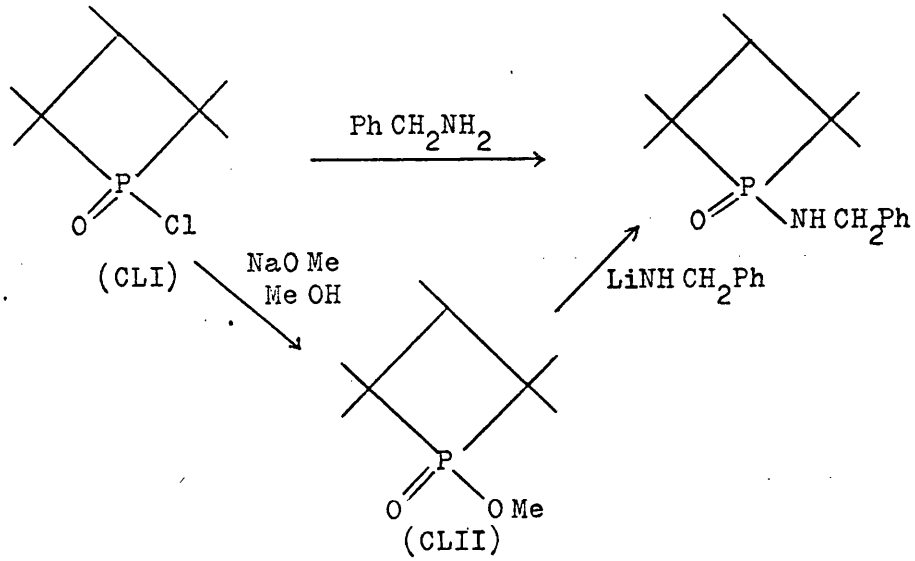
steric course is controlled by the presence of a four membered ring which occupies a relatively strain-free configuration by spanning one apical and one equatorial position in the trigonal bipyramidal intermediate. The nature of the reactants are such that either ring expansion and/or complete ring opening may occur.

Ring expansion, but never ring opening, occurred in the penta-methylphosphetane system. This can be attributed to the high energy barrier for the formation of a tertiary carbanion required for ring opening. Thus if a reaction occurs at all, ring expansion takes place to a group which can accommodate a negative charge.

In the tri- and tetra-methylphosphetane systems, either a CH_2 or a CMe_2 group may reside in the apical position of the intermediate. When the CMe_2 group is apical, ring expansion occurs as in the penta-methylphosphetane system. However, when the CH_2 group is apical, two possibilities were found to occur, either ring expansion, or ring opening to give the primary carbanion followed by protonation. Which of these two processes took place depended upon the ability of the group to which migration occurred to stabilise a negative charge. Thus in the trimethylphosphetane series, the methylene iodide salt hydrolysis and the ethyl propiolate reaction proceeded with ring expansion, whereas treatment of the oxide or the 1-methylphosphetanium salt with sodium hydroxide proceeded with ring opening.

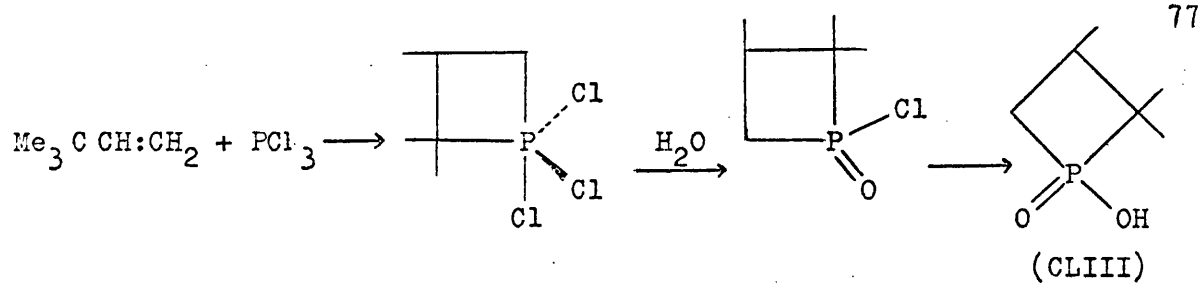
Other Substitution Reactions in Phosphetanes.

The chloropentamethylphosphetane oxide (CLI) made by the preparation of Jungermann and McBride[65] has been found to consist of only one geometrical isomer[66]. Hawes obtained the same pure geometrical isomer of 1-benzylaminopentamethylphosphetane-1-oxide from the reaction of this pure acid chloride (CLI) with two equivalents of benzylamine, as from a two step process *via* the methyl ester (CLII).



As all three substitution reactions were of a similar nature and as the two step process gave the same geometrical isomer as the one step process, then all three reactions were proceeding with retention of configuration at the phosphorus atom.

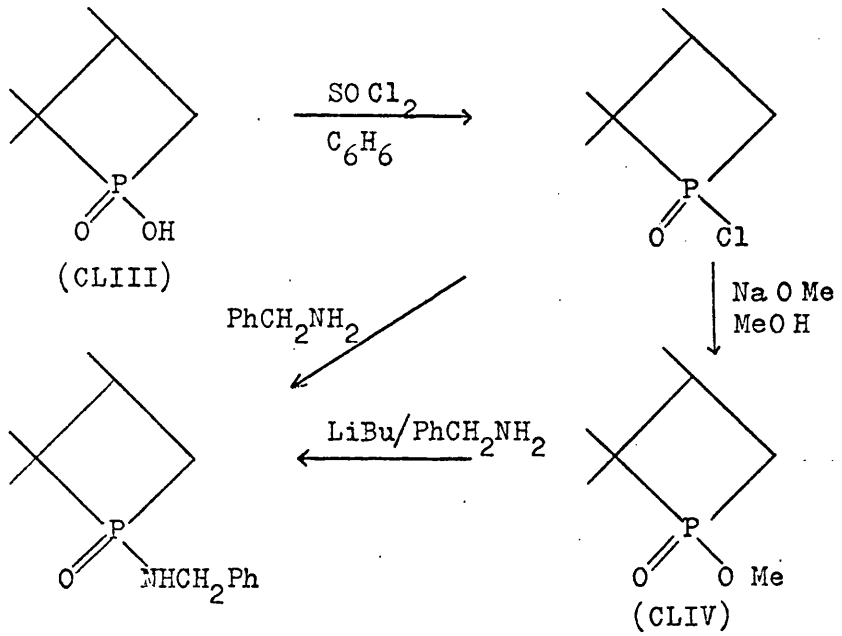
Addition of t-butylethylene to equimolar quantities of phosphorus trichloride and aluminium chloride in methylene chloride, followed by the addition of water, gave the 2,2,3-trimethylphosphetinic acid (CLIII). This result is in marked contrast to the preparation of the pentamethyl acid chloride (CLI) carried out under identical conditions. Obviously the addition of water to the reaction was sufficient to bring about not only decomposition of the trichlorophosphorane to the acid chloride, but also the hydrolysis of the acid chloride to give the phosphinic acid (CLIII).



(CLIII)

This is another example of the enhanced reactivity of the trimethylphosphetane system as compared with the pentamethylphosphetane system[124].

The phosphinic acid (CLIII) was converted to the acid chloride by treatment with thionyl chloride. The corresponding reaction cycle in the trimethylphosphetane system as indicated below was carried out successfully,



However, no information on the stereochemistry of these three reactions could be obtained, as the peaks in the ^{1}H N.M.R. of the acid chloride and the amide proved to be too broad for the estimation of isomer ratios. Isomer ratios could be estimated only in the methyl ester (CLIV) of trimethylphosphetinic acid.

Pentacoordinate Phosphorus Compounds.

Extensive work on pentacoordinate phosphorus compounds has been carried out in the past few years and from this work several general conclusions have been drawn.

1. All structure determinations by electron diffraction and X-ray crystallographic techniques have shown that those pentacoordinate phosphoranes investigated, existed as trigonal bipyramids. The compounds studied included fluorophosphoranes [137] and oxyphosphoranes [100] and pentaphenylphosphorane [98]. Even the stable Wittig intermediate prepared by Birum and Matthews [138] has been shown to have this structure [97]. Thus it has been assumed that all pentacoordinate phosphoranes have the trigonal bipyramidal structure.

2. These structure determinations, together with ^{19}F and ^{1}H N.M.R. investigations, have led to the hypothesis that the more electronegative substituents prefer to occupy an apical position, whilst the more electropositive substituents prefer an equatorial position [139-141].

3. The presence of a four or five membered ring containing the phosphorus atom would enhance the stability of the phosphorane as both rings require a bond angle of approximately 90° at phosphorus and so would prefer to lie apical-equatorial. The X-ray structure determinations so far carried out confirm this proposal [97, 100].

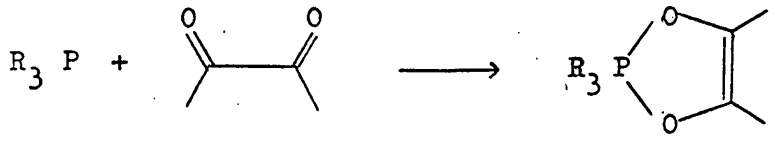
4. In general, pentacoordinate phosphoranes exhibit positive ^{31}P N.M.R. shifts with respect to 85% H_3PO_4.

5. ^{19}F and ^{1}H N.M.R. studies have indicated that in many cases the phenomenon of pseudorotation is taking place.

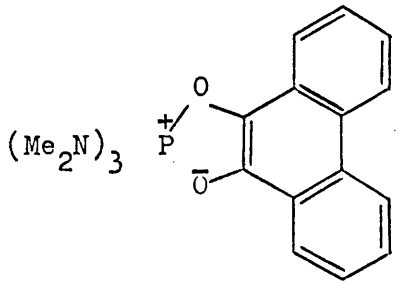
Cyclic Oxyphosphoranes.

Trivalent phosphorus compounds may react with ∝-diketones and o-quinones. The ease of reaction and the nature of the adduct has been found to be dependent to a great extent upon the nature of the substituents upon the phosphorus atom.

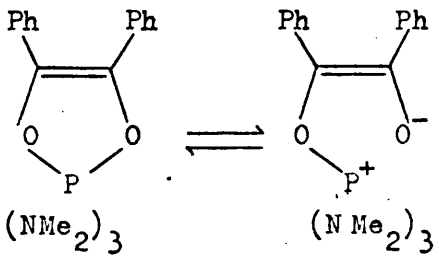
Phosphites such as trimethylphosphite reacted exothermically at room temperature with phenanthraquinone [142], benzil [142] and biacetyl [143, 144] to give stable pentacoordinate phosphoranes containing a five membered ring. In contrast, triphenylphosphine did not react with ∝-diketones and gave only a pentacovalent adduct with phenanthraquinone on heating to 120°C [145]. However, if one or two of the phenyl groups of triphenylphosphine were replaced by alkoxy groups, then pentacovalent adducts were formed with benzil and biacetyl [145, 146].



The reaction between a trivalent phosphorus compound and an ∝-diketone need not necessarily give a pentacoordinate phosphorane; for example, tris(dimethylamino)phosphine with phenanthraquinone gave the dipolar compound (CLV)[147].



(CLV)

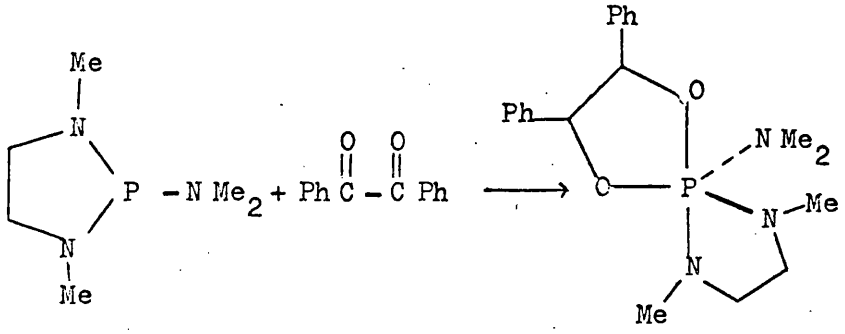


(CLVII) (CLVI)

In fact as equilibrium can exist between the dipolar and the

pentacovalent forms. The structure of the adduct from tris(dimethylamino)phosphine and benzil [148, 149] was found to be dependent upon the polarity of the solvent. Polar solvents aided the formation of the dipolar form (CLVI), whilst non-polar solvents aided the formation of the pentacovalent structure (CLVII) [149,150].

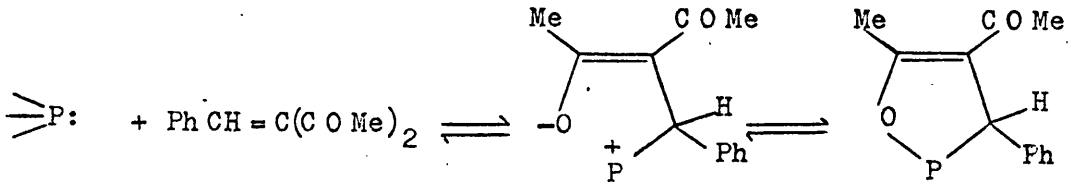
When two of the dimethylamino groups were replaced by alkoxy groups, a pentacovalent adduct only was formed [151]. Further, replacement of tris(dimethylamino)phosphine by the triaminophosphine (CLVIII) containing a five membered ring caused the formation of the corresponding pentacovalent adduct (CLIX), in which the two five-membered rings lay apical-equatorial. No dipolar adduct was detected [152].



(CLVIII) (CLIX)

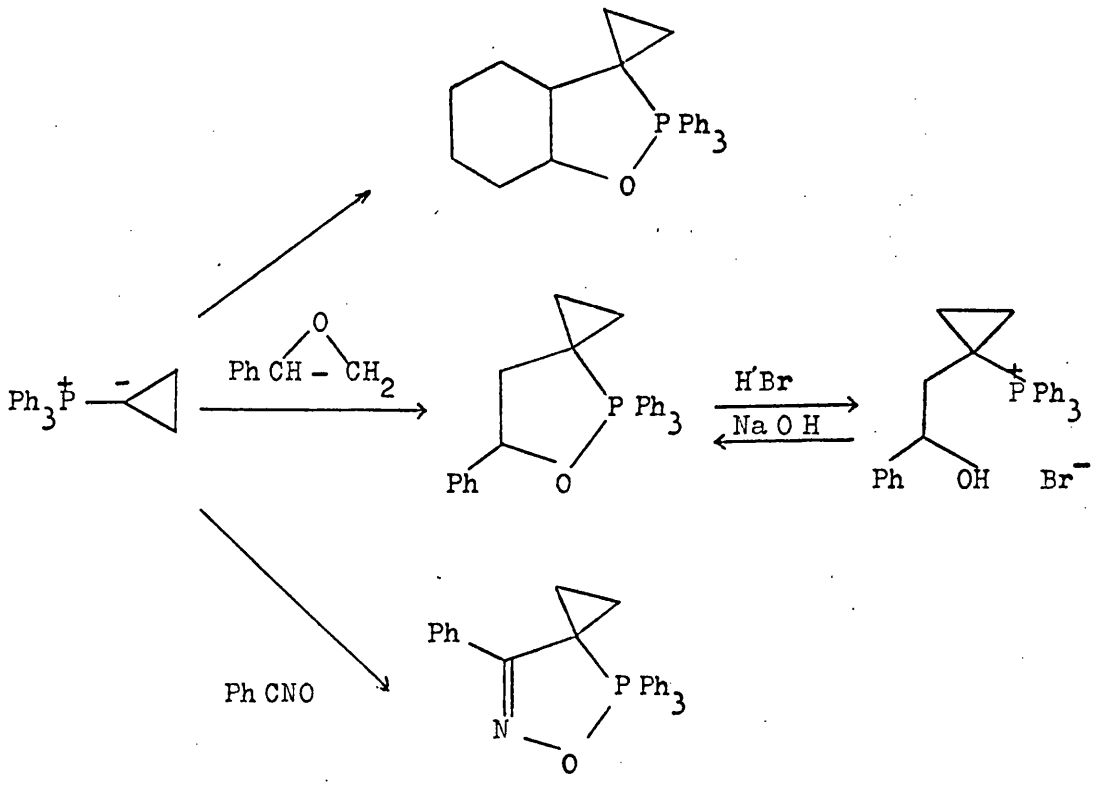
These examples show that pentacoordinate phosphoranes are stabilised by the more electronegative alkoxy substituents and by the presence of five membered rings which can lie apical-equatorial in the trigonal bipyramid.

Trivalent phosphorus compounds have also been found to react with α,β-unsaturated ketones [153-7]. Benzylidene acetylacetone gave pentacovalent adducts (CLX) with phosphites, phosphinites and phosphonites, but gave only dipolar adducts (CLXI) with trialkyl- and dialkylaryl-phosphines [154-6]. Triphenylphosphine gave no adduct [155].



At elevated temperatues, above 70°, the phosphonite and phosphinite pentacovalent adducts gradually formed the dipolar species. At much higher temperatures the dipolar species dissociated to starting materials. Cooling brought about a complete reversal of this process.

In contrast, Bestmann et al. have prepared pentacoordinate phosphoranes containing one oxygen and four carbon functions attached to phosphorus [158,159]. These phosphoranes were prepared by the action of cyclohexene oxide, styrene oxide or phenyl cyanate with cyclopropylidenetriphenylphosphorane.



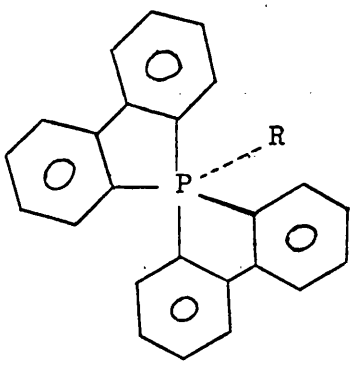
Treatment of any of these three phosphoranes with hydrobromic acid gave the ring opened phosphonium salt, which on treatment with

sodium hydroxide regenerated the phosphorane.

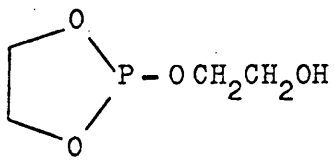
Spirophosphoranes.

Pentacoordinate phosphorus compounds are stabilised by the presence of a ring requiring a bond angle of 90° at phosphorus. Two such rings should further enhance the stability of the phosphorane.

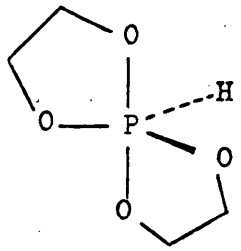
Hellwinkel has made an extensive study of bisbiphenylylenephosphoranes [101] and has found that these compounds are quite stable even with carbon functions occupying the apical positions.



The phosphite ester of ethylene glycol (CLXII) [160] has been shown to exist as the pentacoordinate species (CLXIII) by infrared and ^{31}P and ^{1}H N.M.R. spectroscopy [161].



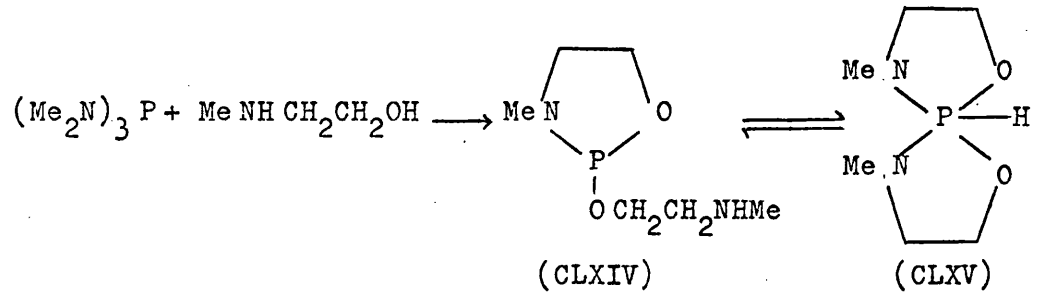
(CLXII)



(CLXIII)

This somewhat unexpected result can be explained by the enhanced stability offered to a pentacovalent phosphorane by two five membered rings. A similar result was obtained by Reetz and Powers [162], who treated tris(dimethylamino)-phosphine with 2-aminoethanol. Their work was confirmed by Burgada et al. who found further that when

N-substituted 2-aminoethanols were used, the trivalent (CLXIV) and pentavalent species (CLXV) were in equilibrium with one another [163].

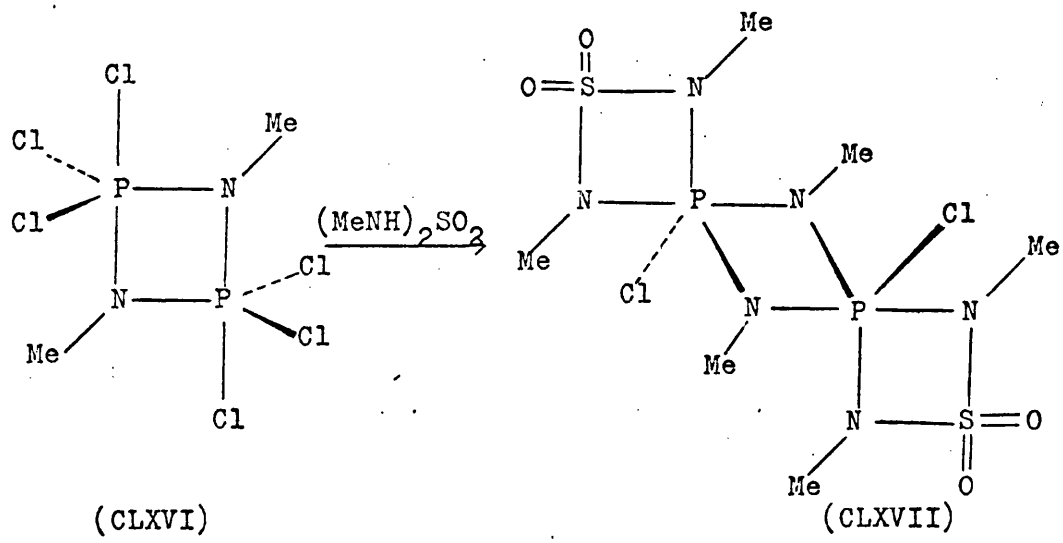


(CLXIV) (CLXV)

Catechol [164,165] and o-aminophenols [166,167] have also been shown to give stable pentacovalent spirophosphoranes.

Phosphoranes Containing Four Membered Rings.

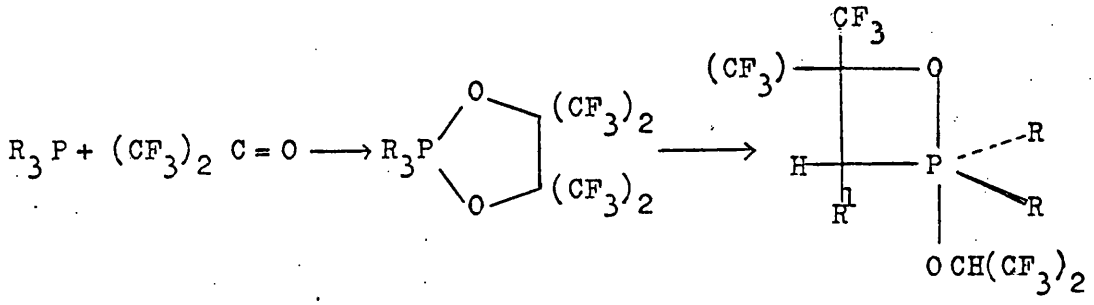
Certain phosphine imines have been shown to exist as dimeric species [168], notably N-methylamino-trichlorophosphorane [169]. The stereochemistry of both phosphorus atoms in this compound (CLXVI) was found to be trigonal bipyramidal with the four membered ring lying apical-equatorial [170]. Becke-Göhring and coworkers [171] have treated this compound (CLXVI) with bis(methylamino)sulphate and obtained a stable spirophosphorane (CLXVII).



(CLXVI) (CLXVII)

Ramirez treated phosphines with hexafluoroacetone and obtained initially a 1,3,2-dioxaphospholane (CLXVIII). On heating this phospholane in benzene, a rearrangement took place with the formation

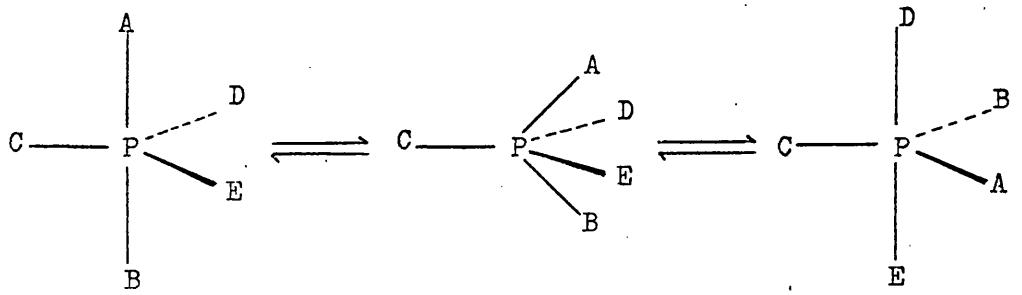
of a stable phosphorane (CLXIX) containing a four membered ring [172].



(CLXVIII) (CLXIX)

Pseudorotation in Pentacoordinate Phosphoranes.

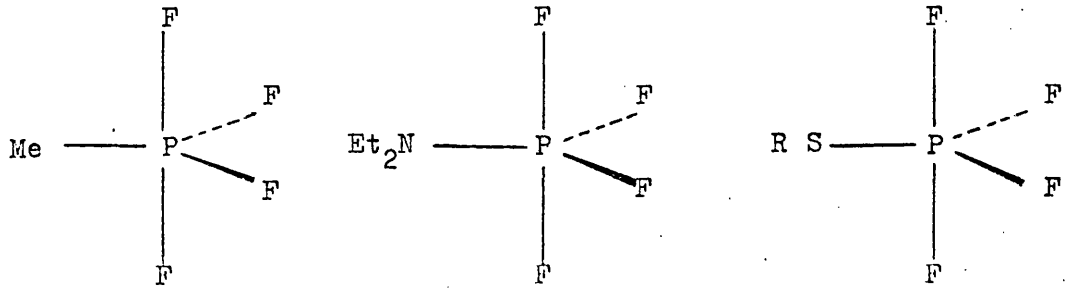
Pseudorotation in a pentacoordinate phosphorane is a process of ligand reorganisation such that one trigonal bipyramid is converted to another trigonal bipyramid via a square pyramidal intermediate [103, 173-5].



Pseudorotation in Fluorophosphoranes.

The process of pseudorotation was first invoked to explain some apparent anomalies in the ^{19}F N.M.R. spectra of various fluorophosphoranes. Though the structure of pentafluorophosphorane was known to be trigonal bipyramidal [137], only one type of fluorine was indicated in the N.M.R. spectrum [176].

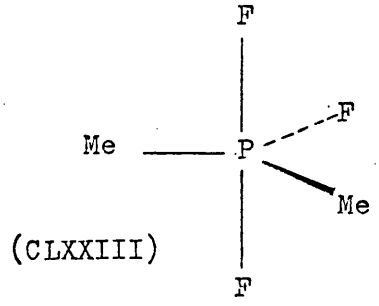
More recent work by Muetterties and Schmutzler [102, 139, 177] on a wide range of substituted fluorophosphoranes has shown some similar anomalies. Methyltetrafluorophosphorane (CLXX), where the methyl group is in the equatorial position of a trigonal bipyramid [137], showed only one type of fluorine at room temperature [139,177]. Likewise diethylaminotetrafluorophosphorane (CLXXI) showed only one type of fluorine at room temperature due to rapid equilibration of the fluorine atoms by pseudorotation. However, on cooling the process of pseudorotation was slowed down and eventually stopped, at which point the ^{19}F N.M.R. spectrum indicated the presence of two types of fluorine atom [140].



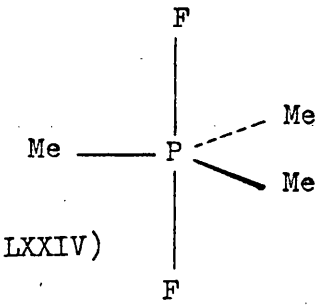
(CLXX) (CLXXI) (CLXXII)

A similar phenomenon was observed on cooling a thioalkyltetrafluorophosphorane (CLXXII). In this case the low temperature N.M.R. spectrum was more complicated than expected, due to the 'freezing' of the P - S bond [178]. All low temperature ^{19}F N.M.R. work of this type indicated an energy barrier to fluorine exchange of between 6 and 12 k.cals./mole.

Further work showed that dimethyltrifluorophosphorane (CLXXIII) and trimethyldifluorophosphorane (CLXXIV) did not pseudorotate and that the methyl groups occupied the equatorial positions.



(CLXXIII)



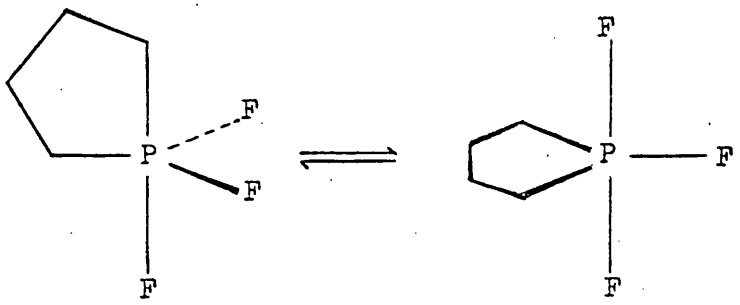
(CLXXIV)

From these and other observations Muetterties and Schmutzler suggested that the more electronegative groups preferred to occupy the apical positions. They found that this hypothesis was valid for fluorophosphoranes containing the following substituents: H, alkyl, aryl, Cl, R_2N, CF_3 and C_2F_5 [139-140].

This hypothesis, together with that of pseudorotation satisfactorily explain the N.M.R. data. The reason for the absence of pseudorotation in phosphoranes (CLXXIII) and (CLXXIV) is that if such a process took place, at least one methyl group would occupy an apical position. According to the above hypothesis, this is an unfavourable process so would be inhibited.

Theoretical calculations [179, 180] agree with the hypothesis of Muetterties. These calculations indicated that the equatorial bonds had more electronegative character than the apical bonds, so the more electronegative groups would occupy the bond with more electropositive character.

One interesting example was the cyclic phosphorane $(CH_2)_4PF_3$ which unlike other dialkyltrifluorophosphoranes pseudorotated at room temperature such that both structure (CLXXV) and (CLXXVI) were present. On cooling to -70°C, pseudorotation was stopped and the phosphorane was found to have the structure (CLXXVI) with the ring lying diequatorial [139].



(CLXXV) (CLXXVI)

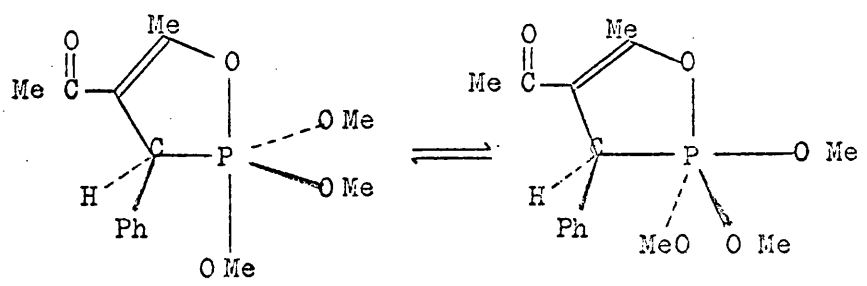
Pseudorotation occurred in this compound at room temperature because the five membered ring was less strained when lying apical-equatorial than when lying diequatorial. Thus the preference of a fluorine atom for an apical position was opposed by the relief of strain in placing the ring apical-equatorial.

Pseudorotation in Oxyphosphoranes.

Several workers have observed apparent anomalies in the ^1H N.M.R. of some oxyphosphoranes which could be explained only if rapid pseudorotation were occurring [154, 181-182].

Although a number of examples of pseudorotation in oxyphosphoranes are known, only two will be given in this section..

Trimethylphosphite formed a stable pentacoordinate adduct (CLXXVII) with 3-benzylidene-2,4-pentanedione [154, 157].

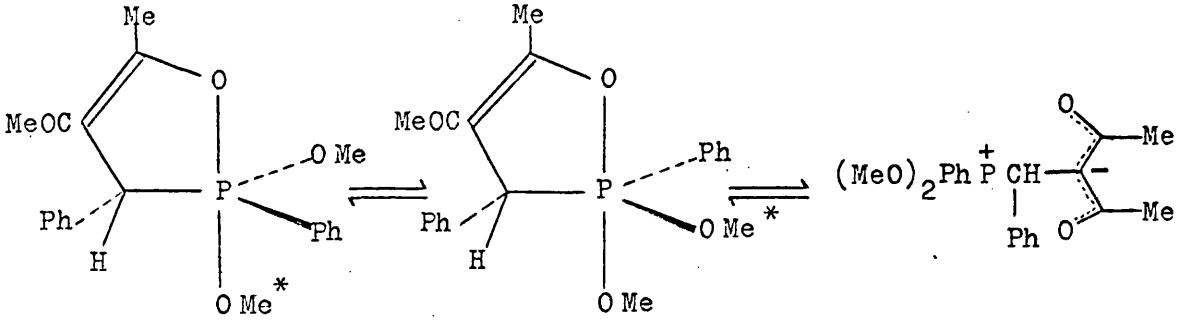


(CLXXVII) (CLXXVIII)

The anticipated structure (CLXXVII) would have electronegative oxygen functions occupying the apical positions with the ring lying apical-equatorial. Pseudorotation of this structure would place either an alkyl group in an apical position, as shown in structure (CLXXVIII) or the ring diequatorial spanning an angle of 120° at phosphorus. The latter process is known to be accompanied by considerable ring strain [183, 184], so would not be expected to occur.

The ^{1}H N.M.R. spectrum was found to be temperature dependent [157]. At room temperature the methoxyl groups were equivalent due to rapid pseudorotation. On cooling a solution of the adduct in deuteriochloroform, pseudorotation was slowed down and eventually stopped, at which point three different methoxyl resonances were shown. One methoxyl lay in an apical position, whilst the other two were in magnetically non-equivalent equatorial positions [154]. At this low temperature, the phosphorane was locked in the most stable conformation (CLXXVII).

The second example is the phosphorane (CLXXIX) formed by the addition of dimethyl phenylphosphonite to 3-benzylidene-2,4-pentanedione.

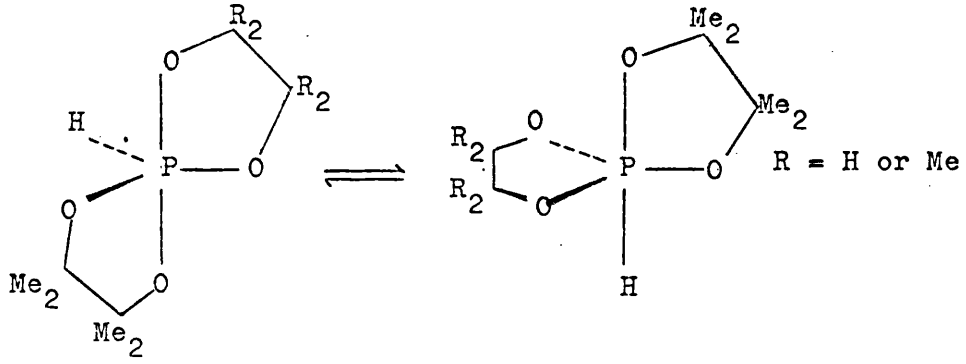


(CLXXIX) (CLXXX) (CLXXXI)

The ^{1}H N.M.R. was again found to be temperature dependent [156, 185-6]. At -11°C. no pseudorotation took place and the cis and trans isomers (CLXXIX) and (CLXXX) were distinguishable in the N.M.R. However, on raising the temperature the rate of pseudorotation gradually increased until at +86° the two isomers were indistinguishable. The two methoxyl groups became equivalent only at higher temperatures, when fission of the ring and formation of a zwitterionic structure (CLXXXI) occurred.

If it is assumed that the ring may not be diequatorial and that alkyl and aryl groups cannot occupy the two apical positions simultaneously, then there is only one process involving four pseudorotations by which structures (CLXXIX) and (CLXXX) may interconvert.

Recent work by Wolf and coworkers[187] on pseudorotation in spirocyclic oxyphosphoranes has shown that the difference in energy between the structure (CLXXXII), where both rings lie apical-equatorial, and structure (CLXXXIII) with one ring diequatorial, was between 15 and 18.4 k.cal./mole depending upon the ring substituents. This meant that the energy barrier to this process would be much greater.

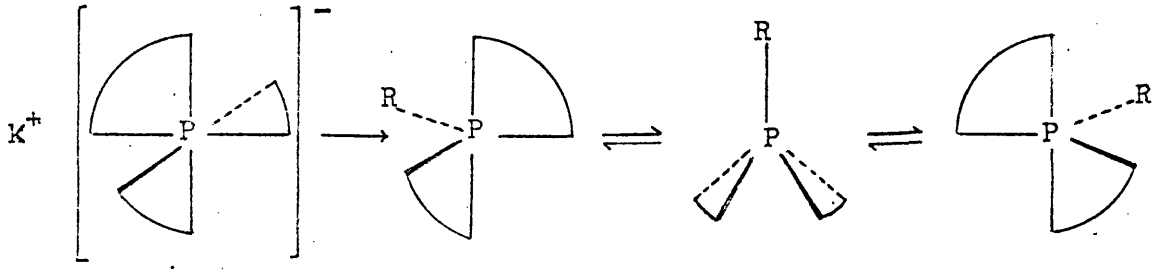


(CLXXXII) (CLXXXIII)

Pseudorotation in Penta-arylphosphoranes.

This field of penta-arylphosphoranes has been pioneered by Hellwinkel and Wittig[89].

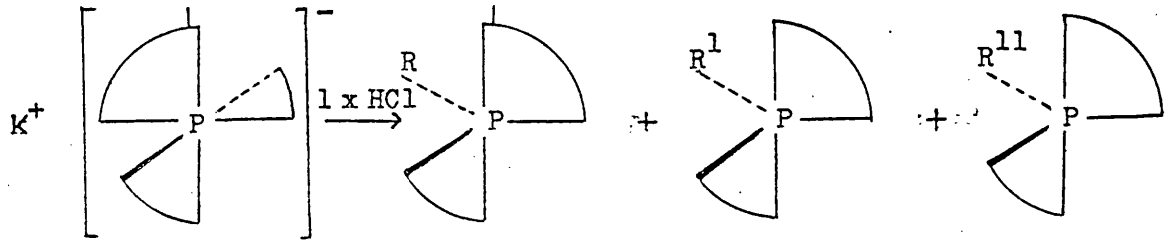
Hellwinkel, in a study of these compounds, has observed the phenomenon of pseudorotation using the techniques of optical activity and ^{1}H N.M.R. spectroscopy. He found that treatment of the trisbiphenylylenephosphate anion (CLXXXIV) with acid gave bisbiphenylylenebiphenyl-2-ylphosphorane (CLXXXV) [101]. In an attempt to prepare an optically active phosphorane, the optical enantiomers of potassium trisbiphenylylenephosphate (CLXXXIV) were separated and were found to have the exceptionally high rotation of $\pm 1930^{o}$ [188]. However, treatment of this optically active salt with an equimolar quantity of hydrochloric acid gave an optically inactive phosphorane (CLXXXV) [101].



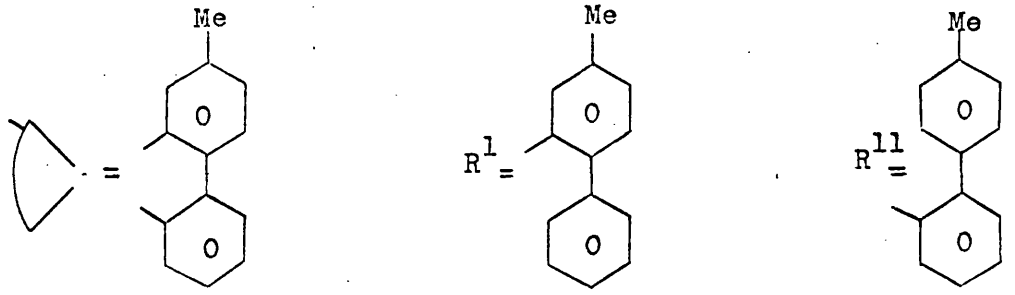
(CLXXXIV) (CLXXXVa) (CLXXXVI) (CLXXXVb)

Though at first it might appear that phosphorane (CLXXXVa) should be optically active, one pseudorotation would give phosphorane (CLXXXVb), its mirror image. Also the square pyramidal intermediate (CLXXXVI) in this pseudorotation process has a plane of symmetry and therefore is optically inactive.

In order to foil this racemisation process, potassium bisbiphenylylene-(4-methylbiphenylylene)-phosphate (CLXXXVII) was prepared and separated into its optical antipodes.

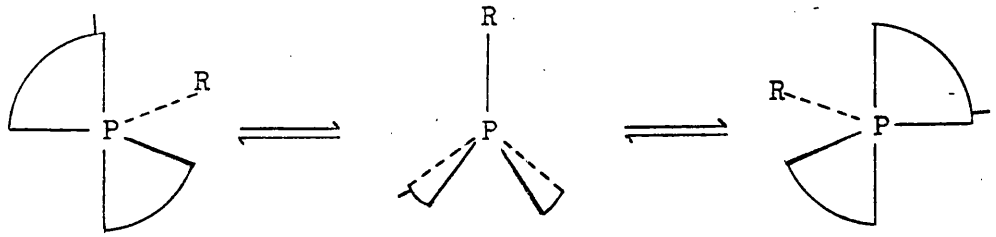


(CLXXXVII) (CLXXXVIII) (CLXXXIX) (CXC)



Treatment of the optically active salt (CLXXXVII) with an equivalent quantity of hydrochloric acid gave the three possible phosphoranes (CLXXXVIII), (CLXXXIX) and (CXC). Phosphoranes (CLXXXIX) and (CXC) were optically inactive as expected, but the phosphorane (CLXXXVIII) was also

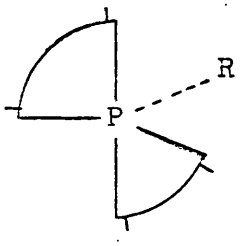
found to be inactive. This was a completely unexpected result for the phosphorane (CLXXXVIII) could only racemise by placing a biphenylylene ring diequatorial. Pseudorotation via a square pyramidal intermediate should not cause racemisation as that intermediate would have no plane of symmetry and would therefore be optically active.



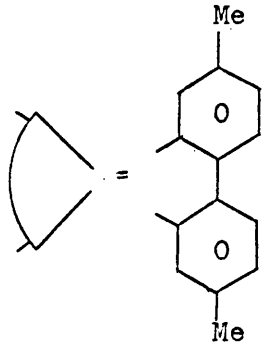
On repeating this reaction with a twofold excess of acid, the phosphorane (CLXXXVIII) was obtained in an optically impure state. This phosphorane was recrystallised to constant optical rotation and was found to be optically stable. Although there is as yet no evidence for the racemisation of this phosphorane, Hellwinkel proposed that the phosphate anion of (CLXXXVII) could decompose by two stereochemically different variations of the same route such that one route produced the optical antipode to that given by the other route.

A fairly extensive ^{1}H N.M.R. study of spirocyclic phosphoranes has recently been carried out [189-191] and has led to the determination of the energy barrier to pseudorotation in these systems.

Variable temperature ^{1}H N.M.R. work carried out on a series of aryl- and alkyl-bis-4,4^{1}-dimethylbiphenylylenephosphoranes (CXCI) has shown that the barrier to pseudorotation was dependent upon the steric bulk of the group R. The value of this energy barrier varied from 12 k.cal./mole when R was of low steric bulk, to 17 k.cal./mole when R was of high steric bulk.



(CXCI)



Pseudorotation in the Hydrolysis of Phosphate Esters.

The results obtained from the hydrolyses of five-membered cyclic phosphates and phosphonates can be satisfactorily explained if the following assumptions are made:

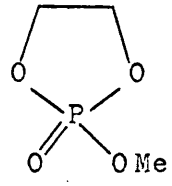
1) Hydrolyses proceed via a trigonal bipyramidal pentacoordinate species.

2) Groups enter at or leave from the apical positions of this species.

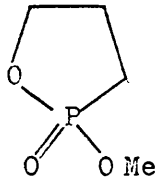
3) Positional exchange in this species can occur by pseudorotation.

4) It is energetically unfavourable for an alkyl group to occupy an apical position.

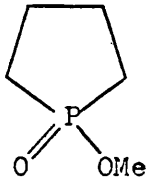
The rates of hydrolysis of methyl ethylene phosphate (CXCII) and of the methyl ester of propylphostonic acid (CXCIII) have been found to be about a million times faster than those of their respective acyclic analogues [123]. However, the products from these two hydrolyses differed. The hydrolysis of the phostonate (CXCIII) proceeded entirely with ring opening, whereas the hydrolysis of methyl ethylene phosphate (CXCII) gave 70% of the ring opened product and 30% ring retention. In comparison, the rate of hydrolysis of the methyl ester (CXCIV) of tetramethylenephosphinic acid was very similar to that of the corresponding acyclic analogue [125].



(CXCII)



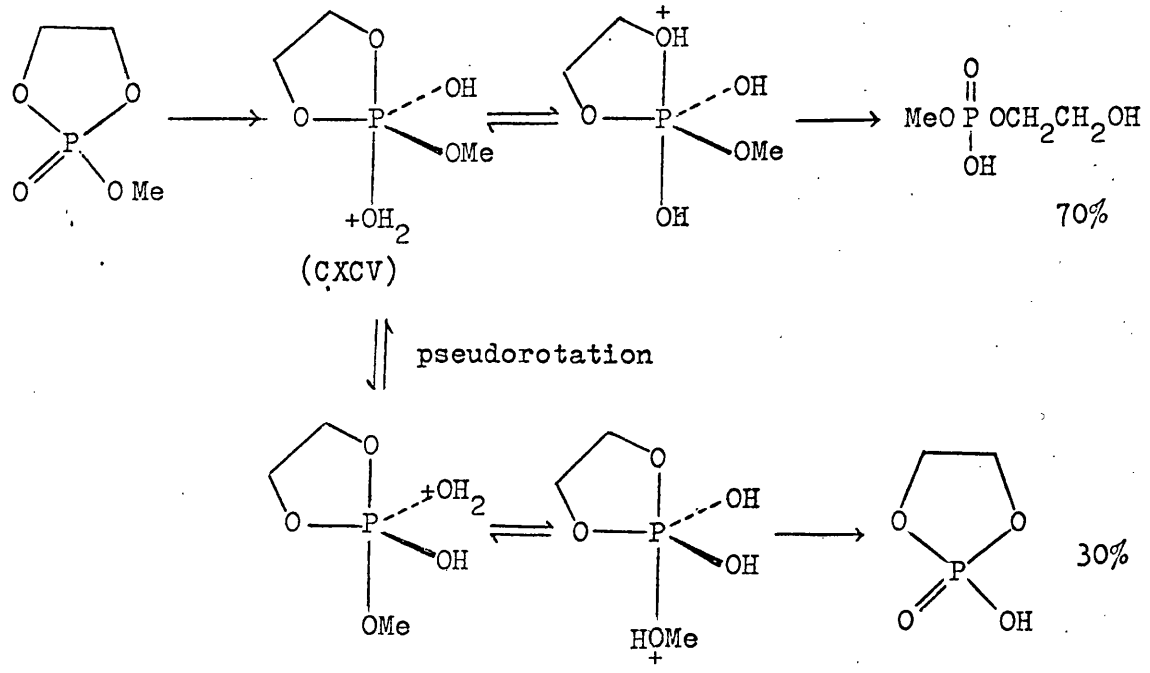
(CXCIII)



(CXCIV)

This enhanced rate of the cyclic phosphate as compared to its acyclic analogue was thought to be due to relief of strain in the ring on forming a trigonal bipyramidal intermediate. This would appear to be an incomplete answer as very little rate enhancement was observed for the ester (CXCIV). These results were interpreted satisfactorily by using the postulates at the beginning of this section[123].

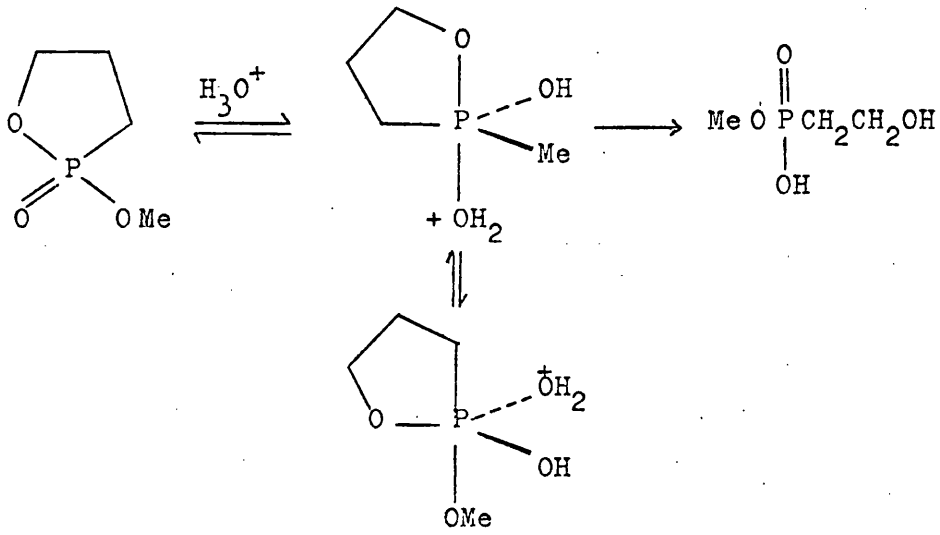
The mechanism for the acid hydrolysis of ester (CXCII) was proposed as the apical attack of water to give the trigonal bipyramidal intermediate with the ring lying apical-equatorial.



Two processes were now possible; either proton migration in intermediate (CXCV) occurred, followed by fission of the ring from an apical position, or intermediate (CXCV) pseudorotated and after proton transfer lost methanol from an apical position to give the ring retained product.

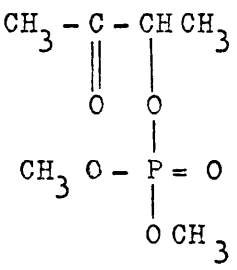
Support for this mechanism was provided by the hydrolysis of the methyl ester of propylphostonic acid (CXCIII) in which the intermediate (CXCVI) was initially formed. This intermediate, after proton transfer,

would readily lose the protonated ring oxygen from an apical position to give the ring opened product. Pseudorotation of this intermediate would place the ring carbon apical and the ring oxygen equatorial, a process energetically less favourable. Thus hydrolysis with retention of the ring would not be expected to occur. This was in fact the case for this reaction was found to proceed completely with ring opening.

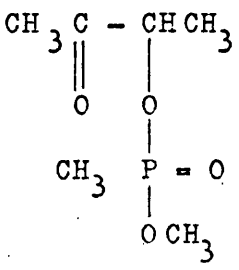


The possible loss of methanol from an equatorial position in the hydrolysis of methyl ethylene phosphate (CXCII) does not occur, for such a process does not take place in the hydrolysis of the phostonate (CXCIII). It has also been stated that such a process would contravene the extended principle of microscopic reversibility[186].

A more recent example of pseudorotation has been reported by Frank and Usher[192], who found that the phosphate (CXCVI) gave acetoin and dimethyl phosphate, whereas the phosphonate (CXCVII) gave methanol on alkaline hydrolysis.



(CXCVI)



(CXCVII)

Pentacoordinate Adducts of Phosphetanes.

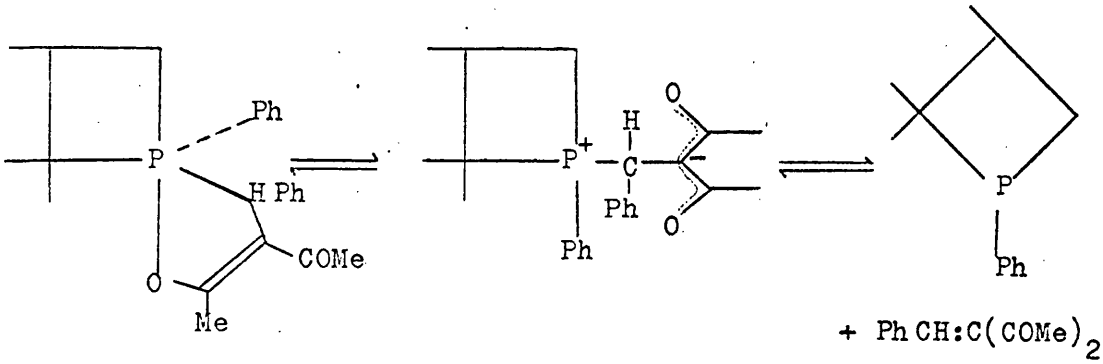
The examples given in the introduction to pentacoordinate phosphoranes showed that such structures were stabilised by the presence of a four or five membered ring spanning a bond angle of 90° at phosphorus. Consequently, the phosphetane ring should enhance the stability of a pentacoordinate phosphorane.

Adducts with Benzylidene Acetylacetone.

Hawes found[66] that cis-pentamethyl-1-phenylphosphetane reacted exothermically with benzylidene acetylacetone to give a 1:1 adduct which was pentacovalent in the solid state, but existed as the dipolar form in solution. At elevated temperatures in o-dichlorobenzene, the dipolar adduct was found to dissociate into the phosphetane and benzylidene acetylacetone.

2,2,3-Trimethyl-1-phenylphosphetane (19:1 isomer ratio) reacted exothermically with benzylidene acetylacetone in benzene, giving a 1:1 adduct (CXCVIII), a composition confirmed by elemental analysis. Unlike the pentamethylphosphetane adduct obtained by Hawes, this trimethylphosphetane adduct (CXCVIII) exhibited identical infrared spectra both in the solid state (nujol mull) and in solution in benzene, the solution spectrum remaining unchanged over a period of 20 hours. A strong absorption at $\nu_{max.}$ 1620 $cm.^{-1}$ indicated the presence of a conjugated carbonyl, whilst the ^{1}H N.M.R. spectrum in benzene at room temperature exhibited two sharp singlets at τ 8.2 and τ 7.42 corresponding to the two different methyl groups on the acetylacetone residue in a pentacoordinate phosphorane. In a more polar solvent, o-dichlorobenzene, at room temperature, these two signals were slightly broader. On raising the temperature, the two peaks broadened until coallescence occurred at about 80°C. Further elevation of temperature brought about

a sharpening of this peak. Cooling the solution brought about the reverse process.



(CXCVIII) (CIC)

The adduct in chloroform exhibited a ^{31}P N.M.R. shift of + 34 p.p.m. (H_3PO_4), a value comparable with those obtained by Ramirez for pentacovalent adducts of phosphites and phosphonites with benzylidene acetylacetone.

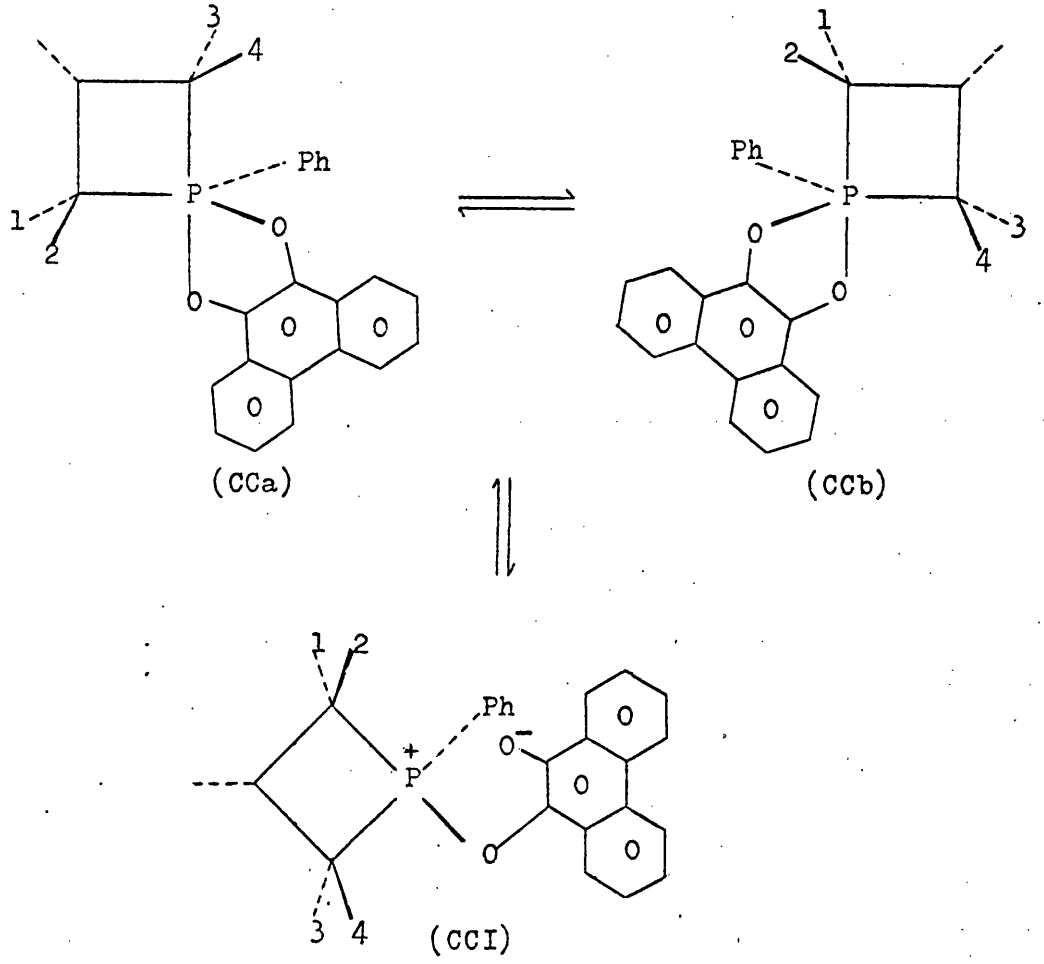
This data showed that the adduct existed solely as the phosphorane (CXCVIII) in the solid state and in non-polar solution. In a more polar solvent at room temperature, a small quantity of the dipolar species (CIC) was present. Increasing the temperature caused an increase in the concentration of this dipolar species, and ultimately its dissociation to starting materials.

This experiment, together with that carried out by Hawes on the pentamethylphenylphosphetane, illustrate the enhancement to pentacoordinate phosphorane formation afforded by the four-membered phosphetane ring, for Ramirez showed [155] that acyclic dialkylarylphosphines gave only the dipolar species with benzylidene acetylacetone.

Adducts with Phenanthraquinone.

Cis-pentamethyl-1-phenylphosphetane reacted exothermically with phenanthraquinone to give a very stable, orange coloured, 1:1 adduct. This adduct exhibited a ^{31}P N.M.R. shift of -0.5 p.p.m. (H_3PO_4) in chloroform, a value very close to that for the phenanthraquinone adduct

of diethylphenylphosphine [193]. The ^{1}H N.M.R. spectrum was found to be almost independent of temperature over the range -60° to + 135°, and exhibited two doublets, each corresponding to two equivalent methyl groups α to the phosphorus atom.



The only variation in the spectrum was observed at the two very extremes of temperature, where slight line broadening occurred.

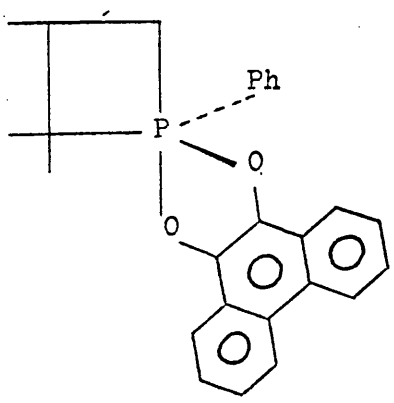
This ^{1}H N.M.R. data could be explained in two ways. Either the adduct was present in the dipolar form (CCI) over the whole temperature range, except at + 135° C where dissociation began to take place and at -60° where the pentacovalent structure (CC) was beginning to form, or the adduct existed as the pentacoordinate phosphorane (CCa), which was pseudorotating rapidly to structure (CCb), thus bringing about equilibration of methyl groups 1 and 3, and 2 and 4. At + 135° formation of the dipolar species was just beginning to occur, whilst at -60° the pseudorotation process was very slow.

The infrared data confirmed that the latter process is the correct one. The infrared spectra of this adduct were identical in both the solid state and in solution in chloroform, having very strong absorptions at $\nu_{max.}$ 1055 $cm.^{-1}$ and 1030 cm^{-1}, which are characteristic of pentacoordinate adducts of phenanthraquinone [142]. These two absorptions are not exhibited by dipolar adducts of phenanthraquinone[147].

2,2,3-Trimethyl-1-phenylphosphetane (4:1 isomer ratio) reacted readily, but not exothermically with 9,10-phenanthraquinone in the minimum quantity of benzene to give a 1:1 adduct. This adduct was not as stable as that from pentamethylphenylphosphetane as it was readily decomposed by water. In solution, dissociation of the adduct to phosphetane and quinone occurred slowly but if left for a sufficient length of time, the insoluble phenanthraquinone crystallised out of solution, thus bringing about complete dissociation.

The infrared spectra of the adduct in the solid state (nujol mull) and in a freshly prepared benzene solution were essentially identical to one another and were almost identical to the spectrum of the pentamethylphenylphosphetane adduct.

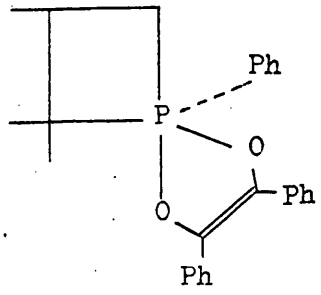
A freshly prepared benzene solution of the adduct exhibited a ^{31}P N.M.R. shift of +3 p.p.m. relative to 85% H_3PO_4. This value was similar to that for the pentamethylphosphetane-phenanthraquinone adduct and together with the infrared data would indicate that the adduct was a pentacoordinate phosphorane (CCII).



(CCII)

Adducts with Benzil.

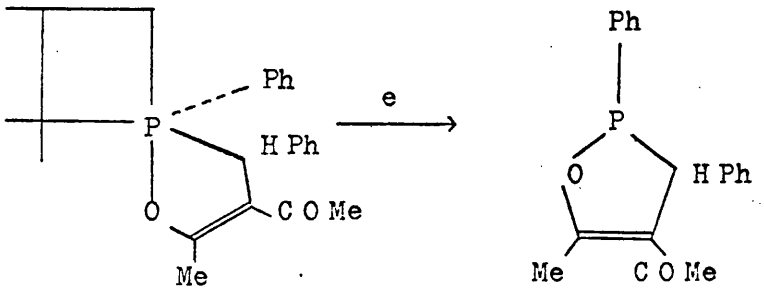
2,2,3-Trimethyl-1-phenylphosphetane reacted with benzil to give a liquid 1:1 adduct which decomposed readily in moist air to benzoin and trimethylphenylphosphetane oxide. This adduct exhibited a ^{31}P N.M.R. shift of +18 p.p.m. (85% H_3PO_4), and had an infrared spectrum characteristic of a pentacovalent adduct of benzil [149]. This spectrosoopic data confirmed that the trimethylphosphetane-benzil adduct was a pentacoordinate phosphorane (CCIII).



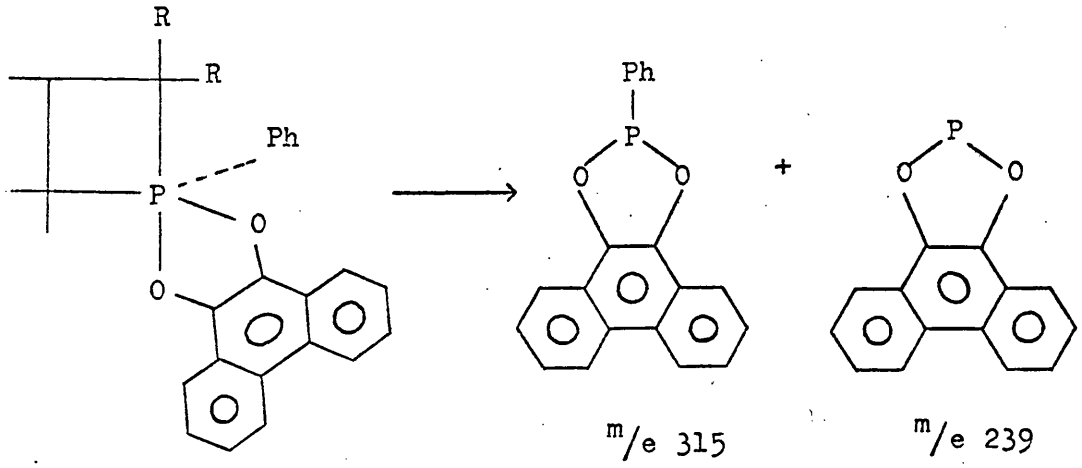
(CCIII)

Mass Spectra of Phosphoranes.

The adducts (CXCVIII), (CC) and (CCII) gave mass spectra which exhibited a characteristic similarity. The major peak in the breakdown pattern of the three adducts corresponded to the species which had lost the carbon skeleton of the phosphetane ring.



(CXCVIII) $^{m}/e$ 380 $^{m}/e$ 296

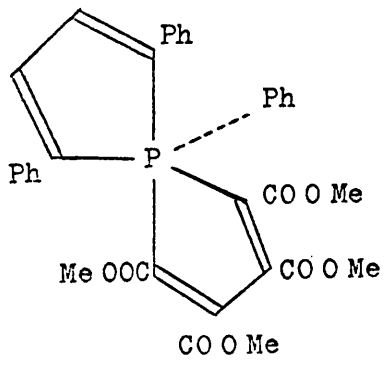


(CC: R = Me, $^{m}/_{e}$ 428)
(CCII: R = H, $^{m}/_{e}$ 400)

It would appear from these observations that the five-membered ring containing one or two oxygen functions is much more stable to electron impact than the four membered phosphetane ring.

Adducts with Dimethyl Acetylenedicarboxylate.

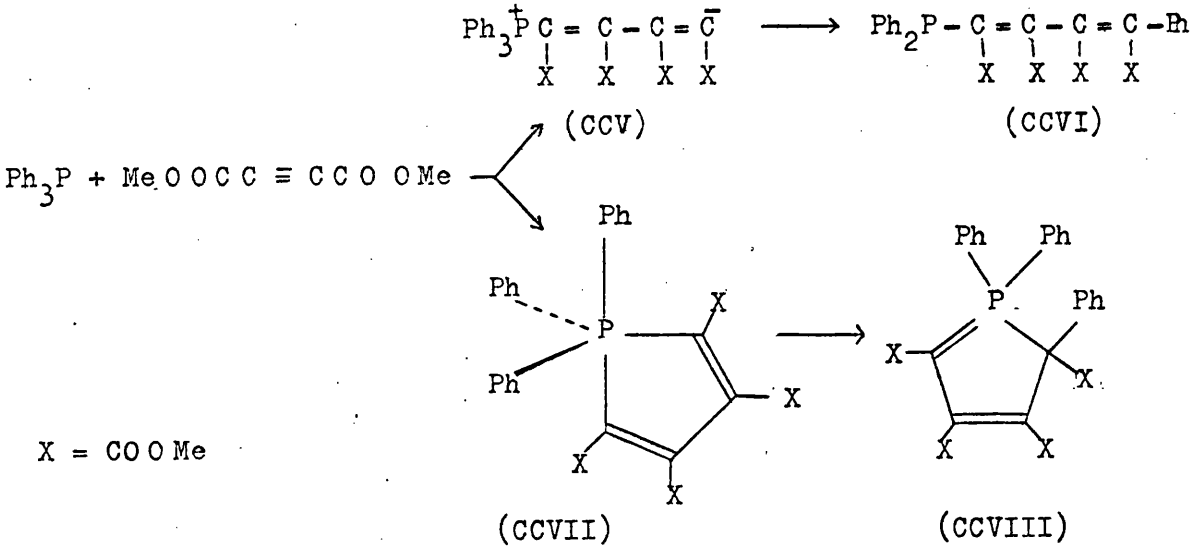
Hughes reported[194] that 1,2,5-triphenylphosphole reacted with dimethyl acetylenedicarboxylate at room temperature to give the penta-coordinate phosphorane (CCIV), which on heating underwent a remarkable rearrangement to a multicyclic phosphine.



(CCIV)

The work of Hellwinkel has shown that spirophosphoranes containing five-membered rings similar to those in structure (CCIV) could be very stable. Thus an attempt was made to prepare adducts similar to (CCIV) from tri- and penta-methyl-1-phenylphosphetane and the acetylenic diester. However, both these attempts proved unsuccessful.

Considerable doubt[195] now surrounds this report of Hughes, especially in the light of Tebby's reinterpretation[196] of an earlier publication[197]. Tebby treated triphenylphosphine with an excess of dimethyl acetylenedicarboxylate and originally reported that phenyl migration from phosphorus to the terminal carbon atom of the Zwitteriomic intermediate (CCV) occurred, giving a phosphine (CCVI). The failure of this phosphine to quaternise was ascribed to the electron withdrawing property of the side chain.



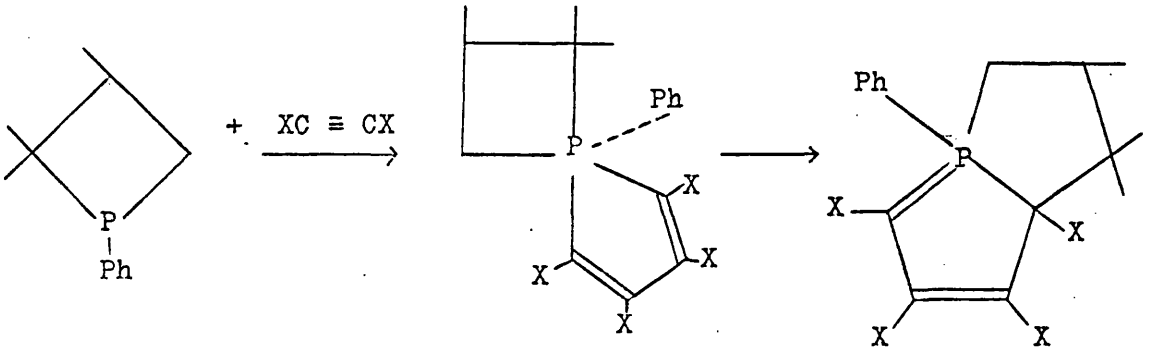
A reinvestigation of this reaction[196] has shown that the product was the ylid (CCVIII). Phenyl migration from phosphorus to the α-carbon took place in the intermediate phosphorane (CCVII), giving the ylid (CCVIII) which exhibited a ^{31}P N.M.R. shift of -48.5 p.p.m. (85% H_3PO_4).

The reaction of 2,2,3-trimethyl-1-phenylphosphetane (19:1 ratio) with a greater than two-fold excess of dimethyl acetylenedicarboxylate in benzene at 0°C. yielded a pale yellow crystalline solid whose elemental analysis corresponded to a 1:2 adduct. This was confirmed by the mass spectrum which showed only two major peaks; one the mass peak for a 1:2 adduct (M), the other for a species (M - COOMe). The infrared spectrum indicated the presence of four different ester groups of which only one was non-conjugated; a P-Phenyl bond was also shown ($\nu_{max.}$ 1430cm.$^{-1}$).

The ^{1}H N.M.R. spectrum was temperature independent and showed four different ester methyl groups and two aliphatic methyl singlets in both benzene and deuteriochloroform solution. The aromatic region of the ^{1}H N.M.R. spectrum in deuteriochloroform contained the characteristic signal for a phenyl group attached to phosphorus.

The infrared spectrum of this adduct from 1800cm.$^{-1}$ to 1100cm.$^{-1}$ bore a very close resemblance to that of Tebby's adduct (CCVIII). Likewise, the four methyl ester resonances in the ^{1}H N.M.R. spectrum of this adduct occurred at almost identical positions to those of Tebby's adduct (CCVIII)[195,196]. A solution of the phosphetane adduct in chloroform exhibited a ^{31}P N.M.R. shift of -76 p.p.m. with respect to 85% H_3PO_4.

The above data and comparative studies indicate that the adduct from 2,2,3-trimethyl-1-phenylphosphetane and dimethyl acetylenedicarboxylate has the structure (CCIX).

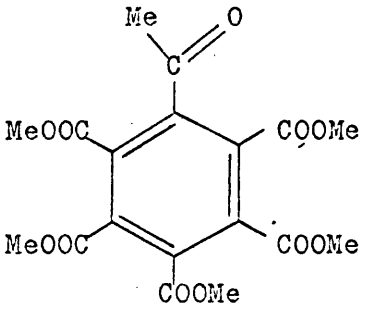


(CCX) (CCIX)

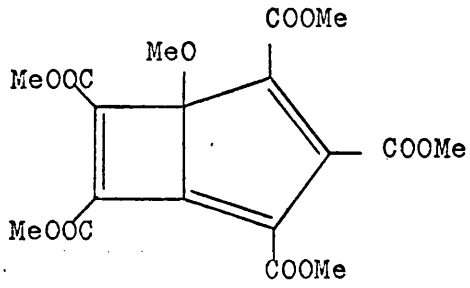
Ring expansion, rather than phenyl migration, took place because such a migration occurs from an apical position in the spirophosphorane (CCX). For the phenyl group to be apical one of the rings must lie diequatorial; a very unfavourable process. No adduct was obtained in which the ring CH_2 group had migrated from phosphorus to the α-carbon atom.

2,2,3,4,4-Pentamethyl-1-phenylphosphetane reacted with excess dimethyl acetylenedicarboxylate in benzene at 0°C, yielding a dark red oil. Chromatography of this oil on silica gave the same oil over a wide range of eluent polarity and an highly crystalline white solid.

Elemental analysis of these crystals showed the absence of phosphorus and gave an elemental formula of $C_{18}H_{18}O_{11}$. This was, in fact, the molecular formula since the mass spectrum gave a mass peak at $^{m}/e$ 410, a value confirmed by molecular weight determination, using vapour pressure osmometry. Only two possible structures, (CCXI) and (CCXII) could be devised to fit this formula.



(CCXI)



(CCXII)

Of these, structure (CCXI) is the more favoured as the compound was found to be unaffected by catalytic hydrogenation and by bromination using bromine in carbon tetrachloride.

The infrared spectrum showed strong absorptions at $\nu_{max.}$ 1742 and 1724cm.$^{-1}$, whilst the ^{1}H N.M.R. spectrum showed that one methyl was different from the rest. This separate methyl singlet occurred at a much lower field (5.68 τ) than that normally expected for a benzoyl methyl or a methyl ether. In structure (CCXI), however, the carboxyl of the acetyl group would be forced out of the plane of the phenyl ring thus placing the methyl group in such an environment between two ortho carbomethoxy groups, that resonance might occur at such a low field. A similar environmental argument may be put forward for the methyl ether (CCXII). The U V spectrum proved inconclusive other than showing that a highly conjugated system was present.

No completely satisfactory mechanism could be devised for the formation of either structure. No trace of this compound could be found in the acetylenic ester, nor was any produced in the reaction of

the trimethylphosphetane with the acetylenic ester.

Conclusion.

With the exception of the reactions with acetylenic esters, the two phosphetanes formed pentacoordinate phosphoranes much more readily than their acyclic analogues and the adducts once formed tended to be more stable. This enhancement in the formation of pentacoordinate adducts rather than dipolar species can be related directly to the preference of the four-membered phosphetane ring to occupy an apical-equatorial position in the trigonal bipyramidal phosphorane.

EXPERIMENTAL.

Instrumentation.

^{1}H N.M.R. spectra were recorded on a Varian A-60 spectrometer, except for the work on the pentamethylphosphetane series, for which a Varian T-60 spectrometer was used. ^{31}P N.M.R. spectra were recorded on a Varian D.A.60 spectrometer. Solution of deuteriochloroform except where otherwise stated.

Mass spectra were determined on an A.E.I. M.S. 9 instrument; in each case the mass peak is given first, followed by those of structural significance.

Molecular weights, where given, were determined on a Mechrolab 301 A Vapour Pressure Osmometer.

Infra-red spectra were recorded on a Perkin-Elmer 237 spectrometer.

Ultra-violet spectra were recorded on a Unicam S.P. 800 spectrometer.

Optical rotations were determined on a Perkin-Elmer 141 polarimeter, using a cell of path length 1 decimeter and a capacity of 5 mls.

G.L.C. analysis was performed on a Perkin-Elmer F 11 instrument, using a 2 metre x $\frac{1}{8}$ " Silicone gum rubber D.E. 120 column.

General Details.

All reactions involving reactants or products susceptible to air or water were carried out in an atmosphere of dry, oxygen-free nitrogen.

Light petroleum had b.p. 60 - 80°C.

Solvents were dried as follows:-

Benzene, methylene chloride, methanol and ethanol were refluxed over calcium hydride and distilled on to molecular sieves.

Petroleum spirit over sodium wire.

Acetone over anhydrous potassium carbonate.

Tetrahydrofuran was dried by refluxing over calcium hydride and distilling on to fresh sodium wire and dry molecular sieves. When

required, a portion was refluxed over and distilled from lithium aluminium hydride immediately prior to use. Diethyl ether when required very dry was purified in a similar fashion. Otherwise it was dried over sodium.

Liquid reagents were distilled before use.

The n Butyl-lithium used was a 2.5N solution in hexane supplied by The Aldrich Chemical Company.

Reactions of Diphenylvinylphosphine with Alkyl Halides.

Diphenylvinylphosphine was prepared by the method of Berlin and Butler[49].

(a) Methyl Iodide.

Quaternisation in benzene at 0°C gave methyldiphenylvinylphosphonium iodide, m.p. 119-121°C (from chloroform-ethyl acetate) (90%), doublet at τ 7.02 (3H, J_{PH} = 14c./sec.), multiplet at τ 2.5-4.0 (3H), and a multiplet at τ 1.5-2.3 (10H). $\nu_{max.}$ 1120, 976, 916, 902cm.$^{-1}$. (Found: C,51.1; H, 4.6; P, 8.9. $C_{15}H_{18}IP$ requires C,50.9; H,4.5; P, 8.8%).

(b) Benzyl Bromide.

The phosphine (2g.) and benzyl bromide (4ml.) were refluxed in benzene (30ml.) for 1 hr. The resulting white solid could not be recrystallised and was therefore precipitated from chloroform by the addition of ethyl acetate, m.p. $\approx$ 240°C (decomp.), $\nu_{max.}$ 1109 cm^{-1}. Molecular weight (ethanol) 2500. N.M.R. showed no benzylic protons and a very broad peak in the aromatic region.

A solution of diphenylvinylphosphine (0.7 g.) and benzyl bromide (0.7 g.) in methanol (20 ml.) was set aside at room temperature for 24 hrs. and then evaporated. Crystallisation of the residue from chloro-

form-ether gave benzyl-2-methoxyethyldiphenylphosphonium bromide (80%), m.p. 157 - 159°C, singlet at τ 6.9 (3H), multiplet at τ 6.1 - 6.73 (4H), doublet at τ 5.2 (2H, J_{PH} = 15c./sec.), singlet at τ 2.84 (5H) and a multiplet at τ 1.8 - 2.6 (10H). $\nu_{max.}$ 1120cm.$^{-1}$.

(Found: C, 63.7; H, 6.0; P, 7.6. $C_{22}H_{24}BrOP$ requires C, 63.6; H, 5.8; P, 7.5%).

When this reaction was repeated in the presence of propionaldehyde (1g.), filtration gave the bisphosphonium salt ethylene-1-(benzyldiphenylphosphonium)-2-(diphenylvinylphosphonium) dibromide (XXXIII), m.p. 325 - 330°C (decomp.), $\nu_{max.}$ 1110cm.$^{-1}$.

(Found: C, 62.8; H, 5.0; Br, 23.2; P, 9.2. $C_{35}H_{34}Br_2P_2$ requires C, 62.1; H, 5.0; Br, 23.6; P, 9.2%).

No N.M.R. was obtained as this salt was insoluble in all solvents tried.

c) Allyl Bromide.

A solution of diphenylvinylphosphine (0.9 g.) and allyl bromide (0.7g.) in methanol (20ml.) was set aside at room temperature for 24 hr. and then evaporated. Recrystallisation of the residue from methanol - ether gave a highly crystalline phosphonium salt (0.16g.), m.p. 289 - 291°, $\nu_{max.}$ 1430, 1130, 1110 and 995cm^{-1}.

(Found: C, 56.65; H, 5.62; Br, 23.52; P, 9.31. $C_{32}H_{38}Br_2O_2P_2$ requires C, 56.8; H, 5.62; Br, 23.67; P, 9.17%).

Quaternisation of Diphenylvinylphosphine with Alkyl Bromides.

The phosphine (2g.) and the alkyl bromide (benzyl bromide, phenacyl bromide, or ethyl bromoacetate) (2g.) in benzene (50ml.) was refluxed for 1 hr. The white solid could not be recrystallised and decomposed above 240°C with shrinkage but without melting. The N.M.R. spectra always showed very broad peaks. Analysis of the product by Volhard titration indicated ca.25% bromide present as bromide ion.

Hydrolysis of the Material Obtained from the Reaction of Diphenylvinylphosphine with Benzyl Bromide.

The material (2g.) in 2N aqueous sodium hydroxide (50ml.) was heated

at 100°C for 2 hrs. On cooling, the products were extracted with methylene chloride, dried, the solvent removed, and the residue was chromatographed on silica. Elution with ether-methanol (50:1) gave benzyldiphenylphosphine oxide (15mg.) m.p. and mixed m.p. 191 - 192°C[51]. Elution with ether-methanol (10:1) gave a colourless glass (1.1 g.) whose N.M.R. and I.R. consisted solely of very broad peaks.

Hydrolysis of the Bisphosphonium salt.

Ethylene-1(benzyldiphenylphosphonium)-2-(diphenylvinylphosphonium) dibromide (XXXIII), (0.12g.) was refluxed in 2N-sodium hydroxide for 2hrs. The products were extracted with methylene chloride and were chromatographed on basic alumina (10g.). Elution with ether-methanol (50:1) (150mls.) gave benzyldiphenylphosphine oxide (25mg.) m.p. and mixed m.p.[51] 191 - 192°C, and elution with ether-methanol (20:1) (150 ml) gave 1,2-bis(diphenylphosphinyl)ethane (39mgs), m.p. and mixed m.p. [198] 268 - 270°C.

Preparation of Dibenzylphenylvinylphosphonium bromide.

Dibenzylphenylphosphine [50] (10.6 g) and β-bromoethyl phenyl ether (9.5 g) in phenol (50 ml.) were heated at 90°C for three days and then slowly added to ether (1500ml.) at 0°C. The resulting solid was purified by precipitation from chloroform by the addition of ether to give dibenzyl-β-phenoxyethyl-phenylphosphonium bromide (60%), m.p. 93 - 94°C. singlet at τ 2.8 (10H), doublet at τ 5.46 (4H, J_{PH} = 15.4c./sec.), multiplet at τ 1.6 - 2.8 (5H), multiplet at τ 2.9 - 3.5 (5H), multiplet at τ 5.45 - 6.0 and τ 6.37 - 6.85 (4H), $\nu_{max.}$ 1113 $cm.^{-1}$, 1248 $cm.^{-1}$. (Found: C, 68.6; H, 5.9; P, 6.1. $C_{28}H_{28}Br$ O P requires C, 68.4; H, 5.7; P, 6.3%).

A suspension of this salt (5g.) in ethyl acetate (40ml.) containing triethylamine (60mg.) was refluxed for ½ hr. and cooled and filtered to give dibenzylphenylvinylphosphonium bromide (84%), m.p. 189 - 190°C, (from chloroform-ethyl acetate), doublet at τ 5.19 (4H, J_{PH} = 16c./sec.), multiplet at τ 2.9 - 3.8 (3H), singlet at τ 2.84 (10H) and multiplet at τ 2.0 - 2.6 (5H). $\nu_{max.}$ 1120 cm^{-1}, 1005 $cm.^{-1}$.

(Found: C, 66.3; H, 5.6; P, 7.9. $C_{22}H_{22}Br$ P requires C, 66.5; H, 5.5, P, 7.8%).

When impure dibenzylphenylphosphine and β-bromoethyl phenyl ether were heated in phenol at 90°C for 48 hrs. and the solution poured into cold ether, crystallisation of the resulting syrup from chloroform-ethyl acetate gave the ethylene-bis(dibenzylphenylphosphonium) dibromide, m.p. 283 - 284°, multiplet at τ 6.7 (4H), multiplet at τ 5.35 (8H), singlet at τ 2.9 (20H) and multiplet at τ 2.0 - 3.3 (10H). $\nu_{max.}$ 1117cm^{-1}. (Found: Br, 21.3; P, 8.4. $C_{42}H_{42}Br_2P_2$ requires Br, 20.8; P, 8.1%). A satisfactory analysis for carbon could not be obtained.

Alkaline hydrolysis gave the two isomers of 1,2,bis(benzylphenylphosphinyl)ethane. The one soluble in benzene had m.p. 204.5 - 205°, m/e 458, 367, 243, singlet at τ 2.7 (10H), multiplet at τ 2.3 - 3.1 (10H), multiplet at τ 6.6 - 6.83 (4H) and multiplet at τ 7.7 - 8.1 (4H), $\nu_{max.}$ 1190 cm^{-1}. 1115 cm^{-1}.
(Found: C, 73.5; H, 6.5; P, 14.1. $C_{28}H_{28}O_2P_2$ requires C, 73.5; H, 6.4; P, 13.6%). The other isomer which was insoluble in benzene had m.p. 281 - 282° (from chloroform - light petroleum) and mass spectrum identical to that of the first compound).

Preparation of β-phenoxyethyldiphenylphosphine.

Diphenylphosphine (9.3 g.) and dry tetrahydrofuran (150 ml.) were refluxed for 2 hours with sodium wire (8g.). The excess of sodium wire was removed from the cooled solution, and β-bromoethyl phenyl ether (11g.) in tetrahydrofuran (20ml.) was slowly added. The solution was evaporated under reduced pressure at 0°C, and the residue, in ether, was washed with water and dried. The resulting solution of the β-phenoxyethyldiphenylphosphine was used immediately.

Oxidation with dilute hydrogen peroxide gave β-phenoxyethyldiphenylphosphine oxide, 94%, m.p. 105 - 106° (from benzene-ether), multiplet at τ 2.7 - 3.4 (5H), multiplet at τ 2.0 - 2.7 (10H), multiplet at τ 6.9 - 7.5 (2H), multiplet at τ 5.4 - 5.9 (2H). $\nu_{max.}$ 1235 cm^{-1}, 1187cm^{-1} and 1123cm^{-1}.
(Found: C, 74.3; H, 6.0; P, 9.7. $C_{20}H_{19}O_2P$ requires C, 74.55; H, 5.9; P, 9.6%).

Quaternisation of β-phenoxyethyldiphenylphosphine with alkyl halides.

(a) Methyl iodide at room temperature gave methyl-β-phenoxyethyldiphenylphosphonium iodide, (86%) m.p. 128-128.5° (from chloroform-ethyl acetate), doublet at τ 7.12 (3H, J = 13.5c/s.), multiplet at τ 5.2-6.3 (4H), multiplet at τ 1.8-2.5 (10H) and multiplet at τ 2.8-3.6 (5H). $\nu_{max.}$ 1245 $cm.^{-1}$, 1123 $cm.^{-1}$.
(Found: C, 56.5; H, 4.9; P, 7.2. $C_{21}H_{22}IOP$ requires C, 56.25; H, 4.9; P, 7.3%).

(b) allyl bromide at room temperature gave allyl-β-phenoxyethyldiphenylphosphonium bromide (21%), m.p. 141-143°(from chloroform-ether), multiplet at τ 1.75-2.7 (10H), multiplet at τ 2.8-3.6 (5H), multiplet at τ 5.35-6.3 (6H), and multiplet at τ 4.3-5.0 (3H). $\nu_{max.}$ 1240$cm.^{-1}$, 1121$cm.^{-1}$, 992$cm.^{-1}$, 950$cm.^{-1}$.
(Found: C, 64.7; H, 5.7; P, 7.4. $C_{23}H_{24}BrOP$ requires C, 64.6; H, 5.6; P, 7.3%).

(c) Phenacyl bromide at room temperature gave phenacyl-β-phenoxyethyldiphenylphosphonium bromide, m.p. 223-224°.(56%), doublet at τ 4.82 (J_{PH} = 14.5c/sec.), multiplet at τ 1.8-3.5 (20H) and multiplet at τ 5.3-6.5 (4H). $\nu_{max.}$ 1672$cm.^{-1}$, 1249$cm.^{-1}$, 1120$cm.^{-1}$.
(Found: C, 66.25; H, 5.3; P, 6.3. $C_{26}H_{26}PO_2Br$ requires C, 66.4; H, 5.2; P, 6.15%).

(d) Ethyl bromoacetate gave ethoxycarbonylmethyl-β-phenoxyethyldiphenylphosphonium bromide (58%), m.p. 107-109° (from methanol-ether), triplet at τ 9.0 (3H, J = 7.5c./sec.), doublet at τ 4.98 (2H, J_{PH} = 13.5c/sec.), multiplet at τ 5.4-6.22 (6H), and multiplet at τ 1.7-3.6 (15H). $\nu_{max.}$ 1735$cm.^{-1}$, 1245$cm.^{-1}$, 1121$cm.^{-1}$.
(Found: C, 60.6; H, 5.5; P, 6.7. $C_{24}H_{26}BrO_3P$ requires C, 60.9; H, 5.5; P, 6.6%).

(e) Benzyl bromide gave benzyl-β-phenoxyethyldiphenylphosphonium

bromide monohydrate, (82%) m.p. 95-97°, broad singlet at τ 7.5 (2H, H_2O), doublet at τ 5.11 (2H, J = 15c/sec.), multiplet at τ 1.9-3.6 (15H) and singlet at τ 2.8 (5H). $\nu_{max.}$ (broad) 3390cm.$^{-1}$, 3450cm.$^{-1}$ and 1636cm.$^{-1}$, 1243cm.$^{-1}$, 1120cm.$^{-1}$.

(Found: C, 65.5; H, 5.6; P, 6.8. $C_{27}H_{26}BrOP.\ 1H_2O$ requires C, 65.45; H, 5.6; P, 6.3%).

The same benzylphosphonium salt was obtained from quaternisation of benzyldiphenylphosphine with β-bromoethylphenyl ether.

Benzyldiphenylvinylphosphonium bromide.

Benzyl-β-phenoxyethyldiphenylphosphonium bromide (2g) was refluxed in ethyl acetate (40ml.) containing triethylamine (60mg) for 1 hr. Reprecipitation of the resulting solid from chloroform by the addition of ether gave benzyldiphenylvinylphosphonium bromide, (62%), m.p. 211-212°, doublet at τ 4.92 (2H, J_{PH} = 15c./sec.), multiplet at τ 3.2-4.0 (3H), singlet at τ 2.81 (5H), and multiplet at τ 2.0-3.0 (10H), $\nu_{max.}$ 1115cm.$^{-1}$, 1000cm.$^{-1}$, 980cm.$^{-1}$.

(Found: C,66.0; H, 5.3; P, 8.0. $C_{21}H_{20}BrP$ requires C, 65.8; H, 5.2; P, 8.1%).

Reaction of Dibenzylphenylvinylphosphonium bromide with Propionaldehyde and Potassium Cyanide in Methanol.

A solution of the phosphonium salt (125mg.), potassium cyanide (29mg.) and propionaldehyde (100mg.) in dry methanol (10ml.) was set aside for three days at room temperature. G.L.C. analysis (D.E. 120 column at 130°) showed the presence of 1-phenylprop-1-ene (31%: c::t::1:4), and 1-cyanopent-2-ene (25%).

Reaction of Triphenylvinylphosphonium Bromide with Potassium Cyanide in Methanol.

A solution of triphenylvinylphosphonium bromide (500mg.) and potassium cyanide (80mg.) in dry methanol (20ml.) was set aside at room temperature for 72 hours. The solvent was removed and the residue was extracted with benzene. Addition of methyl iodide (2ml.) to the benzene

solution gave methyltriphenylphosphonium iodide, (350mg.), m.p. and mixed m.p. [199] 182 - 183°. Acrylonitrile was detected in the methanol solution by infrared spectroscopy.

Reaction of Methyldiphenylvinylphosphonium Iodide with Butyllithium and p-Tolualdehyde.

The phosphonium salt (7.1g.) in dry tetrahydrofuran (100ml.) was stirred at room temperature with 2.5N - butyllithium (8.9mls.) for ½ hr., p-tolualdehyde (3g.) was then added and the solution was set aside for ½ hr. After evaporation of the solvent, the residue in methylene chloride was washed with water, dried, and the solvent removed. Chromatography of the products on basic alumina (180g.) and elution with ether-methanol (20:1) gave p-methylstyryldiphenylphosphine oxide (0.22g.) m.p. 207 - 208° (from benzene - light petroleum ether), $^{m}/_{e}$ 318, 303 and 201. Singlet at τ 7.67 (3H), multiplet at τ 2.0 - 3.56 (16H). $\nu_{max.}$ 1179cm.$^{-1}$, 990cm.$^{-1}$.

(Found: C, 79.1; H, 5.95; P, 9.6).. $C_{21}H_{19}OP$ requires C, 79.2; H, 5.98; P, 9.75%).

Elution with ether-methanol (10:1) gave a brown oil (3.5g.) whose infrared spectrum indicated a phosphonium salt ($\nu_{max.}$ 1120cm.$^{-1}$). Alkaline hydrolysis of this oil yielded the above phosphine oxide.

Reaction of Benzyldiphenylvinylphosphonium Bromide with Butyl-lithium and p-Tolualdehyde.

The phosphonium salt (3.83g.) in dry tetrahydrofuran (100ml.) was stirred at room temperature with 2.5N butyl-lithium (4.0ml.) for ½ hr.. p-Tolualdehyde (1.8g.) was then added and the solution was set aside for 1 hr. After evaporation of the solvent, the residue in methylene chloride was washed with water, dried, and the solvent removed. Chromatography of the products on basic alumina (150g.) and elution with petrol-ether (20:1) gave 4-methyl-stilbene m.pt 118 - 120°, (lit.[200], 119 - 120°). Elution with ether-methanol (33:1) gave trans-1-p-tolyl-2-phenyl-4-diphenylphosphinylbut-1-ene (1.55g.). m.p. and mixed m.p.[27] 160 - 162°.

Elution with ether–methanol (10:1) gave an oily phosphonium salt (2g.) which on alkaline hydrolysis gave the above phosphine oxide and 3-phenylpropyldiphenyl-phosphine oxide m.p. and mixed m.p. 102 – 102.5°C.

Preparation of m-Methylbenzyldiphenyl-1-phenylvinylphosphonium Bromide.

A solution of 1-phenylvinyldiphenylphosphine[27] (5.8g.) and 3-methylbenzyl bromide (4.0g.) in benzene (20ml.) was refluxed for 4 hrs. The solvent was removed leaving an oil, which crystallised on trituration with ether. Recrystallisation from methylene chloride – ethyl acetate – ether gave m-methylbenzyldiphenyl-1-phenylvinylphosphonium bromide (65%), m.p. 141 – 142.5°, singlet at τ 7.9 (3H), doublet at τ 5.1 (2H, J_{PH} = 14c./sec.), and multiplet at τ 1.9 – 3.6 (19H). $\nu_{max.}$ 1113cm.$^{-1}$, 1000cm.$^{-1}$, 963cm.$^{-1}$.

(Found: H, 5.7: P, 6.67. $C_{28}H_{26}BrP$ requires H, 5.56; P, 6.6%)
No satisfactory analysis could be obtained for carbon.

Reaction of m-Methylbenzyldiphenyl-1-phenylvinylphosphonium Bromide with Butyl-lithium and Benzaldehyde.

The phosphonium salt (3.0g.) in dry tetrahydrofuran (100ml.) was stirred at room temperature with 2.5N butyllithium (2.54ml.) for ½ hr., benzaldehyde (2ml.) was added and the solution was set aside for 1 hr. After evaporation of the solvent, the residue in methylene chloride was washed with water, dried and the solvent removed. Chromatography of the products on basic alumina (150g.) and elution with petrol-ether (9:1) gave 3-methyl-stilbene (283 mg.) m.p. and mixed m.p.[201] 54 – 55°.
Elution with ether gave phosphine oxide (LXVI) (250mg.) m.p. 217 – 218° (ethyl acetate – light petroleum), singlet at τ 7.67 (3H), multiplet at τ 7.7 – 8.3 (2H), doublet at τ 5.85 (1H, J = 7.5 c./sec.), and multiplet at τ 1.7 – 3.8 (31H). $^{m}/_{e}$ 600, 399, 201. $\lambda_{max.}$ 268 mμ ε = 12,000 (EtOH). $\nu_{max.}$ 1175, 1120, 825cm.$^{-1}$.

(Found: C, 85.9; H, 6.0; P, 5.25. $C_{43}H_{37}OP$ requires C, 86.0; H, 6.17; P, 5.17%). Molecular weight 603 ($CHCl_3$).
Elution with ether–methanol (50:1) gave 3-methylbenzyldiphenylphosphine

oxide (570 mg.) m.p. 129-130° (from benzene-light petroleum), singlet at τ 7.82, doublet at τ 6.38 (2H, J_{PH} = 14c./sec.), singlet at τ 3.05 (4H), and multiplet at τ 2.06-2.8 (10H). $^{m}/e$ 306, 215, 201. $\nu_{max.}$ 1181cm.$^{-1}$, 1136cm.$^{-1}$, 1120cm.$^{-1}$, 1104cm.$^{-1}$.

(Found: C, 78.6; H, 6.2; P, 10.2. $C_{21}H_{19}OP$ requires C, 78.43; H, 6.2; P, 10.3%).

This oxide is identical to an authentic sample prepared by the Arbusov Reaction of m-methylbenzyl bromide with methyl diphenylphosphinite.

Elution with ether-methanol (20:1) gave 1,2,bis(diphenylphosphinyl)-1-phenylethane (387mg.) m.p. and mixed m.p. ^{202},283-284°.

Reaction of m-Methylbenzyldiphenyl-1-phenylvinylphosphonium Bromide with Butyllithium and Anisaldehyde.

The phosphonium salt (1.7 g.) in dry tetrahydrofuran (100ml.) was stirred at room temperature with 2.5N butyllithium (1.5ml.) for ½ hr., anisaldehyde (1g.) was added and the solution was set aside for ½ hr. After evaporation of the solvent, the residue in methylene chloride was washed, dried and the solvent removed. Chromatography on basic alumina (150g.) and elution with petrol-ether (7:1) gave 3-methyl-4^{1}-methoxy-stilbene (153mg.) m.p. 106.5-107.5°C (from ethanol).

(Found: C, 86.55; H, 7.2. $C_{16}H_{16}O$ requires C, 86.6; H, 6.7%).

Elution with ether gave the phosphine oxide (LXVII) (50mg). m.p. 227-228°C (from ethyl acetate), singlet at τ 7.67 (3H), singlet at τ 6.1 (3H), doublet at τ 5.9 (1H, J_{PH} = 9.0c./sec.), and multiplet at τ 1.7-3.8 (28H) $^{m}/e$ 630, 429, 201. $\lambda_{max.}$ 267 mμ and 272mμ, ε = 20,000 and 19,600 respectively. $\nu_{max.}$ 1245, 1170, 1118, 1030, 827cm.$^{-1}$.

Elution with ether-methanol (50:1) gave 3-methylbenzyldiphenylphosphine oxide (150mg) m.p. and mixed m.p. 128-129°C.

Elution with ether-methanol (20:1) gave 1,2-bis(diphenylphosphinyl)-1-phenylethane (152mg.) m.p. and mixed m.p. ^{202}, 283-284°C.

Hydrolysis of Methyldiphenylvinylphosphonium Iodide.

The phosphonium salt (1g.) in 2N aqueous sodium hydroxide (40ml.) was heated at 100°C for 2 hr. On cooling, the products were extracted with methylene chloride, the solvent removed and the residue chromatographed on silica. Elution with ether-methanol (20:1) gave methyldiphenylphosphine oxide (47%) m.p. and mixed m.p.[203], 107 - 109°C. Elution with methanol gave an intractable yellow oil (220mgs).

Hydrolysis of Benzyldiphenylvinylphosphonium Bromide.

The phosphonium salt (0.75g.) in 2N aqueous sodium hydroxide (40ml) was heated at 100°C for 4 hrs. On cooling, the products were extracted with methylene chloride, dried, and the solvent removed and the residue chromatographed on silica (20g.). Elution with ether-methanol (50:1) gave diphenyl-3-phenylpropylphosphine oxide (180mg.), m.p. 102 - 103° (from benzene-light petroleum), multiplet at τ 7.1 - 8.3 (6H) and multiplet at τ 2.0 - 3.0 (15H). $^{m}/_{e}$ 320, 215, 105. $\nu_{max.}$ 1180cm^{-1}.

(Found: C, 78.4; H, 6.6; P, 9.4. $C_{21}H_{21}OP$ requires C, 78.5; H, 6.56; P, 9.7%).

This compound was identical to a sample prepared by hydrogenation of cinnamyldiphenylphosphine oxide.

Elution with ether-methanol (20:1) gave diphenylvinylphosphine oxide (100mg.) m.p. and mixed m.p.,[49], 114 - 115°C.

Hydrolysis of this phosphonium salt in ethanolic sodium hydroxide solution gave 2-ethoxyethyldiphenylphosphine oxide[63] m.p. and mixed m.p., 66 - 66.5°. (Elution with ether-methanol (50:1) on a silica column).

The nitrogen flowing over the reaction was bubbled through bromine. Work up of the bromine yielded 2,4,5-tribromotoluene m.p. 112 - 113°C (from Ethanol).

Hydrolysis of β-Phenoxyethyltriphenylphosphonium Bromide.

The phosphonium salt (600mg.) in 2N aqueous sodium hydroxide was heated at 100°C for 2 hr. The products were extracted with methylene chloride, dried, the solvent removed and chromatography of the residue on silica (20g.). Elution with light petroleum-ether (1:1) gave phenol

(30mg.) m.p. and mixed m.p. 43°. Elution with ether gave 1-phenylethyldiphenylphosphine oxide (65mg.) m.p. 140 - 141°C (from cyclohexane) m/e 306, 201, quartet at τ 8.41 (3H, J_{PH} = 16c./sec. J_{HH} = 7.5c./sec), multiplet at τ 6.1-6.6 (1H) and multiplet at τ 1.84-3.0 (15H). $\nu_{max.}$ 1180cm^{-1}, 1120cm^{-1}.

(Found: C, 78.2: H, 6.3: P, 9.7. $C_{20}H_{19}OP$ requires C, 78.4; H, 6.2; P, 10.1%). This oxide was found to be identical to an authentic sample synthesised by the addition of methyl iodide to benzylidenediphenylphosphine oxide.

Elution with ether-methanol (33:1) gave triphenylphosphine oxide (36mg.) m.p. and mixed m.p. [205], 153-154°C. Elution with ether-methanol (10:1) gave ethylenebis(diphenylphosphine oxide) (172mg.) m.p. and mixed m.p. [198] 269-270°C.

Hydrolysis of this salt in aqueous ethanolic sodium hydroxide gave only 2-ethoxyethyldiphenylphosphine oxide (90%) m.p, and mixed m.p. [63], 66-67°C.

Hydrolysis of Triphenylvinylphosphonium Bromide.

The phosphonium salt (1g.) in 2N aqueous sodium hydroxide (40ml.) was heated at 100°C for 2 hrs. On cooling, the products were extracted with methylene chloride, dried, the solvent removed and the residue chromatographed on silica. Elution with petrol (40-60°C)-ether (20:1) gave triphenylphosphine in trace amounts. Elution with ether gave 1-phenylethyldiphenylphosphine oxide (55mg.7%) m.p. and mixed m.p. 139-141°C. Elution with ether-methanol (33:1) gave triphenyl phosphine oxide (53mg. 7%) m.p. and mixed m.p. [205], 154-155°C. Elution with ether-methanol (10:1) gave ethylenebis(diphenylphosphine oxide) (500mg. 83%), m.p. and mixed m.p. [198] 268-269°C. G.L.C. analysis of the reaction mixture (D.E. 120 column) at 100°C showed the presence of styrene.

Hydrolysis of this phosphonium salt in ethanolic sodium hydroxide gave 2-ethoxyethyldiphenylphosphine oxide.

Hydrolysis of 2-Bromoethyltriphenylphosphonium Bromide.

The phosphonium salt (1g.) in 2N aqueous sodium hydroxide was heated at 100°C for 2 hr. On cooling, the products were extracted with methylene chloride, dried, the solvent removed, and the residue chromatographed on basic alumina (30g.). Elution with petrol (40 - 60°C) ether (7:1) gave triphenylphosphine (43%), m.p. and mixed m.p. [206], 80°C. Elution with ether - methanol (50:1) gave triphenylphosphine oxide (34%) m.p. and mixed m.p. [205], 154 - 155°C. Elution with ether-methanol (20:1) gave ethylenebis(diphenylphosphine oxide) (21%) m.p. and mixed m.p. [198], 268 - 270°. The bromine trap for the evolved gases yielded p-dibromobenzene.

The phosphonium salt (2.0g.) in 2N aqueous sodium hydroxide (30ml.) and ethanol (20ml.) was refluxed for 2 hr. On cooling, the products were extracted with methylene chloride, dried, the solvent removed, and the residue chromatographed on basic alumina (30g.). Elution with petrol (40 - 60°C)-ether (4:1) gave triphenylphosphine (0.87 g. [m] 5%) as the only product. The bromine trap to detect evolved gases yielded only p-dibromobenzene (72mg.).

Hydrolysis of the salt obtained from the quaternisation of an 'old' sample of β-phenoxyethyldiphenylphosphine oxide with benzyl bromide.

The salt (2g.) which usually had a melting point of above 275°C was treated with 2N sodium hydroxide (50ml.) at 100°C for 2 hrs. On cooling, the products were extracted with methylene chloride, dried, the solvent removed and the residue chromatographed on alumina (60g.). Elution with ether - methanol (50:1) gave benzyldiphenylphosphine oxide, m.p. and mixed m.p. 191 - 2°C. Elution with ether - methanol (20:1) gave ethylene bis(diphenylphosphine oxide). m.p. and mixed m.p. 268 - 269°C.

Reaction of Very Dilute Sodium Hydroxide with Triphenylvinylphosphonium Bromide.

A solution of the phosphonium salt (367mg.) in 0.01N sodium hydroxide solution (10ml.) was set aside at room temperature for 7 days. The aqueous solution was extracted with methylene chloride, which was dried and the solvent removed, leaving a residual oil which crystallised on standing. Recrystallisation from acetone gave 2-hydroxyethyltriphenylphosphonium bromide (91%) m.p. and mixed m.p.[18], 216 - 217°C.

Preparation of 2,2,3-Trimethyl-1-phenylphosphetane-1-oxide.

A solution of 3,3-dimethylbut-1-ene (23g.) in dry methylene chloride (80ml.) was added dropwise to a stirred solution of aluminium chloride (33.3g.) and dichlorophenylphosphine (45g.) in methylene chloride (150ml.) at 0°C. After stirring for a further three hours, water (150ml.) was added slowly dropwise, whilst maintaining the temperature below 20°C. The organic layer was separated, washed with 0.25N sodium hydroxide solution, water, dried, and the solvent removed, leaving an oil which slowly crystallised. Chromatography on basic alumina (500g.) and elution with ether (4 l.) gave a mixture of the two geometrical isomers of 2,2,3-trimethyl-1-phenylphosphetane-1-oxide in 19:1 ratio. (54%), m.p. 85 - 86.5° (from light petroleum) $^{m}/e$ 208, 166, 125, 108, ^{1}H N.M.R. of major component ($CDCl_3$), doublet at τ 8.62 (3H, J_{PH} = 17c/sec.) doublet at τ 8.91 (3H, J_{HH} = 7.5c/sec.) doublet at τ 9.13 (3H, J_{PH} = 20c/sec.), multiplet at τ 6.7 - 8.3 (3H) and multiplet at τ 1.9 - 2.6 (5H). Major component in benzene, doublet at τ 8.71 (3H, J_{PH} = 16.5c./sec.), doublet at τ 9.21 (3H, J_{HH} = 5.0c./sec.) and doublet at τ 9.38 (3H, J_{PH} = 19.25c./sec.). Minor component (C_6H_6) doublet at τ 8.64 (3H, J_{PH} = 17.0c./sec.). ^{31}P N.M.R. (C_6H_6) - 44.0 p.p.m. (85% H_3PO_4). ν max. 1202, 1187, 1156, 1105, and 820 $cm.^{-1}$.

The isomers could be separated neither by chromatography nor by fractional crystallisation.

Reduction of 2,2,3-Trimethyl-1-phenylphosphetane-1-oxide[1].

Method (a)

The phosphetane oxide (10.4 g.) in dry benzene (70 ml.) was added dropwise to a stirred solution of trichlorosilane (20.55 g.) and pyridine (11.9 g.) in dry benzene (80 ml.). After four hours, the solution was cooled to 0°C, and 2N sodium hydroxide (80 ml.) was added slowly dropwise. The organic layer was separated, washed, dried and the solvent removed. Distillation of the residue gave a mixture of the two geo-

metrical isomers of 2,2,3-trimethyl-1-phenylphosphetane in 19:1 ratio. b.p.94°/0.6 m.m. (61%).

Method (b).

Trichlorosilane (6.75 g.) in benzene (30ml.) was added to a solution of triethylamine (5g.) and the phosphetane oxide (10.4 g.) in benzene (100ml.). After stirring for four hours the solution was cooled to 0°C and 2N sodium hydroxide solution (80 ml.) was added slowly dropwise.

The organic layer was separated, washed and dried, and the solvent removed. Distillation of the residue gave a mixture of the two geometrical isomers of 2,2,3-trimethyl-1-phenylphosphetane in a ratio varying from 1:1 to 3:1, b.p. 94°/0.6 m.m. (65%).

^{31}P N.M.R. (C_6H_6) -1.3 and + 3.1 p.p.m. (85% H_3PO_4)

Preparation of 1-Benzyl-2,2,3-Trimethyl-1-phenylphosphetanium Bromide.

Quaternisation of the phosphetane with benzyl bromide in benzene gave 1-benzyl-2,2,3-trimethyl-1-phenylphosphetanium bromide (100%) m.p. 206 - 217° (from chloroform - ethyl acetate). Major isomer showed doublet at τ 8.75 (3H, J_{HH} = 7c/sec.) doublet at τ 8.62 (3H, J_{PH} = 22c./sec), doublet at τ8.04 (3H, J_{PH}= 21c./sec.), multiplet at τ 6.0 - 7.6 (3H), multiplet at τ 4.8 - 5.1 (2H) and multiplet at τ 1.5 - 3.0 (10H). In CF_3COOH, multiplet at τ 4.8 - 5.1 collapsed to a doublet at τ 5.80 (2H, J_{PH} = 12c./sec.). Minor isomer showed doublet at τ 8.12 (3H, J_{PH} = 21c./sec.), and doublet at τ4.91 (2H, J_{PH}= 14c./sec.).

(Found: C, 62.73; H, 6.58; P, 8.4. $C_{19}H_{24}BrP$ requires C, 62.80; H, 6.61; P, 8.54%).

No change in isomer ratio occurred during quaternisation.

Hydrolysis of 1-Benzyl-2,2,3-Trimethyl-1-phenylphosphetanium Bromide.

The salt (0.4 g.) in 0.1 N sodium hydroxide solution (10 ml.) was set aside for 72 hours at room temperature. The solution was extracted with methylene chloride (3x), which was dried and the solvent removed, leaving an oil which slowly crystallised.

^{1}H N.M.R. analysis of the crude product showed that the salt (19:1) had given 2,2,3-trimethyl-1-phenylphosphetane-1-oxide (95%) in a ratio greater than 19:1, but which could not be determined exactly. The salt (4:1) gave the oxide in approximately 19:1 ratio.

The two isomeric oxides were not interconvertible under the conditions of hydrolysis.

Alkaline Hydrolysis of 1-Benzyl-2,2,3-Trimethyl-1-phenylphosphetanium Bromide.

A fractional crystallisation of the phosphetanium bromide (23g.) from chloroform-ethyl acetate gave in the final fraction (0.4 g.) a mixture of the two geometrical isomers of the salt in approximately 1:3 ratio.

This phosphetanium salt (0.4 g.) was hydrolysed in sodium hydroxide solution at 90°C for one hour. The solution was diluted with cold water, and extracted with methylene chloride. The organic fractions were dried, the solvent removed and the residue chromatographed on basic alumina. Elution with ether-methanol (50:1) gave a mixture of the two isomers of 2,2,3 trimethyl-1-phenylphosphetane-1-oxide (89%) in 7:3 ratio.

Oxidation of 2,2,3-Trimethyl-1-phenylphosphetane.

Oxidation of the phosphetane in benzene solution with dilute hydrogen peroxide solution gave 2,2,3-trimethyl-1-phenylphosphetane-1-oxide (100%). The ratio of isomers in the oxide are the same as in the phosphetane for both 19:1 and 4:1 ratios.

Wittig Olefin Synthesis using 1-Benzyl-2,2,3-Trimethyl-1-phenylphosphetanium Bromide.

Method (a)

The phosphetanium salt (1.1g.) (19:1 ratio) and benzaldehyde (1g.) were added to a solution of sodium (0.07g.) in very dry ethanol (20ml.) and the solution was set aside at room temperature for four days. The solvent was removed and the residue in methylene chloride was washed with water, dried, and the solvent again removed. The residue was chromatographed on alumina (65g.) and elution with petrol (40-60) gave stilbene (cis:trans::1:4) (63%). Elution with ether-methanol (50:1) gave 2,2,3-trimethyl-1-phenylphosphetane-1-oxide (91%) in 19:1 isomer ratio, approximately.

Method (b).

The phosphetanium salt (0.9 g.) was stirred with 2.5 N butyllithium (1 ml.) in dry ether (50 ml.) for ½ hr. at room temperature. Benzaldehyde (0.8 ml.) was added and the solution was stirred for a further 1½ hr. The solvent was removed and the residue in methylene chloride was washed with water, dried, and the solvent again removed. Chromatography of the residue on basic alumina (60g.) and elution with petrol (40-60) gave stilbene. Elution with ether-methanol (50 : 1) gave 2,2,3-trimethyl-1-phenylphosphetane-1-oxide, m.p. and mixed m.p. 85 - 86°C.

The phosphetanium salt (19:1) gave stilbene (73%) and phosphetane oxide (94%) with isomer ratio 19:1. However, the salt (4:1) gave stilbene (85%) and the phosphetane oxide (90%) with isomer ratio 9:1.

Reaction of Phenyllithium with 2,2,3-Trimethyl-1-phenylphosphetane-1-oxide.

A solution of 2,2,3-trimethyl-1-phenylphosphetane-1-oxide (1.0 g.) and 1.3 N phenyllithium (3.6 ml.) in dry ether (40 ml.) was stirred for fifteen minutes at 0°C. Methyl iodide was added and the solution was set aside for half an hour. The solvent was removed and the residue

in methylene chloride was washed with water, dried, and the solvent again removed. The residue was chromatographed on silica (40 g.). Elution with ether-methanol (100:1) gave 1,1,2-trimethylpropyldiphenylphosphine oxide, (14%) (purified by sublimation at 130°C/1.m.m) m.p. 155-157°C, doublet at τ 9.1 (6H, J_{HH} = 6.5c./sec.), doublet at τ 8.8 (6H, J_{PH} = 15.5c./sec.), multiplet at τ 7.69-8.4 (1H), and multiplet at τ 1.7-2.8 (10H), $^{m}/e$ 286, 244, 201, 168, 125. ν max. 1200, 1175, 1120, 1100 and 1088 cm^{-1}.

(Found: C, 75.6; H, 8.28; P, 10.6. $C_{18}H_{23}OP$ requires C, 75.53; H, 8.04; P, 10.84%). Elution with ether methanol (33.1) gave an oil containing at least two phosphine oxides which could not be separated. $^{m}/e$ 300, 286, 244, 201, 181, 140. ν max. 1300, 1200, 1180, 1115, 900, 885 cm^{-1}.

Reaction of 2,2,3-Trimethyl-1-phenylphosphetane-1-oxide with sodium hydroxide solution.

The oxide (1 g.) in 2N sodium hydroxide solution (40 ml.) and ethanol (10 ml.) was refluxed for 72 hours. On cooling and dilution, the alkaline solution was extracted with methylene chloride to remove unreacted oxide. The aqueous layer was then acidified and the opaque solution was extracted with methylene chloride until the aqueous layer was clear. The combined organic fractions were dried and the solvent removed, leaving an oil which slowly solidified. Recrystallisation from water gave 1,1,2-trimethylpropylphenylphosphinic acid (88%) m.p. 91-93° C., $^{m}/e$. 452, 367, 267, 226, 210, 183, 141, doublet at τ 9.16 (6H, J_{HH} = 7c./sec.), doublet at τ 9.07 (6H, J_{PH} = 17c./sec.) multiplet at τ 2.15-2.8 (5H), and broad singlet at τ -1.95 (1H). ν max. 1220, 1150, 1110, 970, 780, 761, and 705 cm^{-1}.

(Found: C, 63.42; H, 8.44; P, 13.44. $C_{12}H_{19}O_2P$ requires C, 63.73; H, 8.4; P, 13.72%).

Preparation of 1-Iodomethyl-2,2,3-Trimethyl-1-phenylphosphetanium Iodide.

2,2,3-Trimethyl-1-phenyl-phosphetane (19:1) (2g.) and methylene iodide (4g.) in benzene (30ml.) were refluxed for 5 hours. The pale yellow solid was filtered off and washed with methylene chloride to give a white solid of 1-iodomethyl-2,2,3-trimethyl-1-phenylphosphetanium iodide (60%), m.p. 214 - 215°C (with decomposition)(from n-butanol). ν max. 1440, 1122, 850, 809, 760, and 695 $cm.^{-1}$.
(Found: C,33.82; H,4.21; I, 54.80; P, 6.84. $C_{13}H_{19}I_2P$ requires C, 33.9; H, 4.13; I, 55.23; P, 6.74%).

Alkaline Hydrolysis of 1-Iodomethyl-2,2,3-Trimethyl-1-phenylphosphetanium Iodide.

The phosphetanium salt (1 g.) in 2N sodium hydroxide solution (30ml.) and ethanol (2ml.) was heated at 100° for 3 hours. On cooling and dilution with water, the solution was extracted with methylene chloride. The combined organic layers were dried, the solvent removed, and the residue chromatographed on basic alumina (20 g.). Elution with ether-methanol (100:1) gave an oil consisting of the geometrical isomers of 2,2,3-trimethyl-1-phenylphospholane-1-oxide and 3,4,4-trimethyl-1-phenylphospholane-1-oxide (73% overall yield), b.p. 115°/1.0 m.m. $^{m}/e$. 222, 207, 182, 168, 140, 125, 108. Multiplet at τ 7.3 - 9.67, and multiplet at τ 2.1 - 2.7 in the ratio of 14 : 5. ν max. 1440, 1185, 1150, 1119 and 1096 $cm.^{-1}$.
(Found: H, 8.55; $C_{13}H_{19}OP$ requires H, 8.56%. Satisfactory analyses for carbon and phosphorus could not be obtained.)

Reaction of 2,2,3-Trimethyl-1-phenylphosphetane with Ethyl Propiolate.

Ethyl propiolate (0.5 g.) in ether (10 ml.) was added dropwise to a solution of the phosphetane (1g.) in moist ether (25ml.) at 0°C, and the mixture was stirred for 3 hours. The solvent was removed and the residue chromatographed on silica (25 g.). Elution with ether gave

5-ethoxycarbonylmethyl-3,4,4-trimethyl-1-phenylphospholane-1-oxide (150mg.) b.p. 140°C/2 m.m. $^{m}/_{e}$ 308, 293, 279, 263, 247, 235, 224, 209, 195, and 108, triplet at τ 9.0 (3H, J_{HH} = 7.0c/sec.), multiplet at τ 8.7 - 9.3 (8H), singlet at τ 7.87 (3H), multiplet at τ 7.12 - 7.48 (4H), quartet at τ 5.92 (2H, J_{HH} = 7c/sec.), and multiplet at τ 2.0 - 2.6 (5H). $\nu_{max.}$ 1732, 1440, strong broad absorptions 1260 - 1160, 1115, 1040 and 1035 $cm.^{-1}$.

(Found: H, 8.5; P, 9.88, $C_{17}H_{25}O_3P$ requires H, 8.12; P, 10.07%. A satisfactory analysis for carbon could not be obtained.)

Elution with ether-methanol (20 : 1) gave 5-ethoxycarbonylmethyl-2,2,3-trimethyl-1-phenylphospholane-1-oxide (715mg), b.p. 120°C/2 m.m. $^{m}/_{e}$. 308, 263, 235, 224, 195, multiplet at τ 8.66 - 9.38 (12H) multiplet at τ 6.95 - 8.5 (6H), quartet at τ 6.1 (2H, J_{HH} = 7c/sec.), and multiplet at τ 2.0 - 2.65 (5H). $\nu_{max.}$ 1730, 1437, strong broad absorptions 1280 - 1160, 1120, 1040 and 860 $cm.^{-1}$.

(Found: H, 8.4; P, 9.6. $C_{17}H_{25}O_3P$ requires H, 8.12; P, 10.07%. A satisfactory analysis for carbon could not be obtained.)

Reaction of 2,2,3-Trimethyl-1-phenylphosphetane with dimethyl acetylene dicarboxylate.

A solution of dimethyl acetylene dicarboxylate (1.7 g.) in dry benzene (25 ml.) was added dropwise to a stirred solution of the phosphetane (0.8 g.) in dry benzene (25ml.) at 0°C. The red solution was stirred for a further 1 hour when the solvent was removed. Solidification of the residue on trituration with light petroleum occurred. Recrystallisation from diethyl ether gave yellow-brown crystals of the 2:1 adduct (44%) m.p. 215 - 217°C. $^{m}/_{e}$. 476, 417 and 109, singlet at τ 8.45 (3H), singlet at τ 8.98 (3H), doublet at τ 8.73 (3H, J_{HH} = 6c/sec.), singlet at τ 7.13 (3H), singlet at τ 6.46 (3H), singlet at τ 6.35 (3H), singlet at τ 6.02 (3H) and multiplet at τ 2.1 - 2.67 (5H). ^{31}P N.M.R. ($CHCl_3$) -75.6 p.p.m. (85% H_3PO_4) $\nu_{max.}$ 1745, 1715, 1690, 1660, 1515, 1440, 1330, 1255, 1224, 1207, 1180, 1136, 1109, 1095, and 1090 $cm.^{-1}$.

(Found: C, 60.39%; H, 6.05%; P, 6.19. $C_{24}H_{29}O_8P$ requires C, 60.5; H, 6.10; P, 6.5%.)

The residual red oil was chromatographed on silica, but no other products could be isolated.

Reaction of 2,2,3-Trimethyl-1-phenylphosphetane with 9,10-Phenanthraquinone.

The phosphetane (1g.) and 9,10-phenanthraquinone (1.0 g.) in benzene (½ml.) were stirred for 24 hours. Trituration of the yellow oil with cold dry petrol (40 - 60°C) yielded the 1:1 adduct (98%) m.p. 156 - 160°C (decomposition), $^m/_e$ 400, 330, 316, 239, and 180. In CCl_4 doublet at τ 9.0 (3H, J_{HH} = 6c/sec.), doublet at τ 8.68 (3H, J_{PH} = 21c/sec), doublet at τ 8.48 (3H, J_{PH} = 18c/sec.), multiplet at τ 6.34 - 7.23 (2H) and multiplet at τ 1.4 - 2.87 (13H). ^{31}P N.M.R. (C_6H_6) at -3.1 p.p.m. (85% H_3PO_4). $\nu_{max.}$ 1636, 1340, 1115, 1060, 1035, 960 and 800 $cm.^{-1}$.

(Found: C, 78.0; H, 6.14; P, 7.5. $C_{26}H_{25}O_2P$ requires C, 78.0; H, 6.25; P, 7.75%).

Reaction of 2,2,3-Trimethyl-1-phenylphosphetane with Benzylidene Acetylacetone.

Benzylidene acetylacetone (10g.) was added dropwise to a stirred solution of the phosphetane (1g.) in dry benzene (25ml.) at 0°C. After the exothermic reaction had ceased, the solution was refluxed for 2 hours. The solvent was removed and the residue crystallised on standing, giving the 1:1 adduct (89%), m.p. 147 - 150° (from ethyl acetate), $^m/_e$ 380, 296, 192, 180, multiplet at τ 7.3 - 9.55 (12H), broad singlet at τ 8.16 (3H), broad singlet at τ 7.59 (3H), doublet at τ 5.62 (1H, J_{PH} = 11.5c/sec.), and multiplet at τ 2.34 - 3.2 (10H). Elevated temperature N.M.R. in o-dichlorobenzene, low temperature work in d_6-acetone. ^{31}P N.M.R. ($CHCl_3$) at + 33.6 p.p.m. (85% H_3PO_4). $\nu_{max.}$ 1620, 1125, 1090, 970, 937, and 690 $cm.^{-1}$. In benzene ν máx. 1635, 1530, 1123, 1092, 980 and 937 $cm.^{-1}$.

(Found: C, 75.71; H, 7.78; P, 8.3. $C_{24}H_{29}O_2P$ requires C, 75.79; H, 7.63; 8.16%).

Preparation of 2,2,3-Trimethylphosphetinic acid or (1-Hydroxy-2,2,3-Trimethylphosphetane-1-oxide.

3,3,-Dimethylbut-1-ene (8.7 g.) was added dropwise to a solution of phosphorus trichloride (13.8g.) and anhydrous aluminium chloride (13.3g) in dry methylene chloride (150ml) at 0°C. After stirring the solution for a further 2 hours, water (80ml) was added slowly dropwise, whilst keeping the temperature well below 25°C. The organic layer was separated and the aqueous layer was extracted three times with methylene chloride. The combined organic fractions were dried, the solvent removed and the residue distilled in vacuo, giving 1-hydroxy-2,3,3-trimethylphosphetane-1-oxide (74%), b.p. 173-174°C/1.3 m.m. multiplet at τ 6.68-8.94 (6H) singlet at τ -2.6 (1H), doublet at τ 8.7 (3H, J_{PH} = 20c/sec.) and doublet at τ 8.8 (3H, J_{PH} = 20c/sec). $\nu_{max.}$ 1255, 1220, 980 and intense broad band (S) at 940-900 cm^{-1}.

(Found: C, 49.01; H, 8.90; P, 20.72. $C_6H_{13}O_2P$ requires C, 48.64, H, 8.78; P, 20.94%).

Preparation of 1-Chloro-2,2,3-Trimethylphosphetane-1-oxide.

A solution of 1-hydroxy-2,2,3-trimethylphosphetane-1-oxide (10g.) and thionyl chloride (23g.) in benzene (170ml.) was refluxed for 18 hours when the evolution of sulphur dioxide and hydrogen chloride had ceased. The benzene and excess thionyl chloride were removed and the residue was distilled in vacuo, giving 1-chloro-2,2,3-trimethylphosphetane-1-oxide (8.2g.) b.p. 110°C/0.9 m.m. $\nu_{max.}$ 1255, 1218, 1090, 820 and 632 $cm.^{-1}$.

Preparation of 1-Benzylamino-2,2,3-Trimethylphosphetane-1-Oxide.

A solution of 1-chloro-2,2,3-trimethylphosphetane-1-oxide (1g) and benzylamine (1.3g.) in dry ether (45ml.) was set aside at room temperature for 1 hour. Benzylamine hydrochloride was filtered off and the filtrate was washed with 0.1N sodium hydroxide solution (20ml.), water, dried and the solvent removed. The residual oil was chromatographed on basic alumina (20g.). Elution with ether gave 1-benzylamino-2,2,3-trimethyl-

phosphetane-1-oxide (96%) m.p. 71-72° and 77-78° (from diethyl ether-petroleum spirit (40-60°C)). In CCl_4, doublet at τ 9.0 (3H, J_{PH} = 19.5c/sec.), doublet at τ 9.04 (3H, J_{PH} = 17c/sec.), doublet at τ 9.04-9.2 (3H), multiplet at τ 7.3-8.56 (3H), quartet at τ 6.02 (2H, J_{PH} = 10c/sec. J_{HH} = 5c/sec.), multiplet at τ 4.0-4.58 (1H), and multiplet at τ 2.54-3.1 (5H). Addition of a trace of acid caused a collapse of the quartet at 6.02 to a doublet at τ 6.0 (J_{PH} = 10c/sec.). In benzene, doublet at τ 8.71 (3H, J_{PH} = 18.0 c/sec.), doublet at 8.73 τ (3H, J_{PH} = 19.0 c/sec.) and quartet at τ 9.02 (3H, J_{PH} = 1c/sec, J_{HH} = 6.5 c/sec.). $\nu_{max.}$ 3145, 1195, 1160, 1100, 1070 and 1030 $cm.^{-1}$. (Found: C, 65.84; H, 8.75; N, 5.93; P, 13.29. $C_{13}H_{20}NOP$ requires C, 65.83; H, 8.44; N, 5.91; P, 13.08%).

Preparation of 1-Methoxy-2,2,3-Trimethylphosphetane-1-oxide.

1-Chloro-2,2,3-trimethylphosphetane-1-oxide (6.0g.) was added dropwise to an equivalent quantity of sodium methoxide in methanol (35 ml.). The solution was stirred for 15 hours when the solid sodium chloride was filtered off. The solvent was removed leaving a solid and a liquid. Dry petroleum spirit (40-60°C) was added and the white solid was filtered off. The solvent was removed from the filtrate and the residue was distilled under reduced pressure, giving a mixture of the two geometrical isomers of 1-methoxy-2,2,3-trimethylphosphetane-1-oxide b.p. 80-86°C/7m.m., doublet at τ 6.25 (3H, J_{PH} = 10c/sec) for the major component and doublet at τ 6.26 (3H, J_{PH} = 10c/sec.) for the minor component. $\nu_{max.}$ 1254, 1222, 1040, 1030 and 840 $cm.^{-1}$.

The white solid filtered off (1g.) had m.p. greater than 335°C. In CF_3COOH, multiplet at τ 7.06, - 8.0, broad doublet at τ 8.51 (J = 4c/sec) and broad doublet at τ 8.88 (J = 5c/sec.) in the ratio of 1:2:3.

$\nu_{max.}$ broad band centred at 3340, 1180, 1162, 1110, 1060 and 1035 $cm.^{-1}$.

Reaction of 1-Methoxy-2,2,3-Trimethylphosphetane-1-oxide with Butyllithium and Benzylamine.

1-Methoxy-2,2,3-trimethylphosphetane-1-oxide (0.9 g.) in dry ether (10ml.) was added dropwise to a stirred solution of 2.5N butyllithium (5.0ml.) and benzylamine (1.22g.) in dry ether (30ml.) at room temperature. After stirring for a further hour, 2N hydrochloric acid (5ml.) was added. The organic layer was separated, dried, the solvent removed and the residue chromatographed on silica (35g.). Elution with ether-methanol (20:1) gave 1-benzylamino-2,2,3-trimethylphosphetane-1-oxide (25%) identical to an authentic sample.

Preparation of 2,2,3,3-Tetramethyl-1-phenylphosphetane-1-oxide.

A solution of 2,3,3-trimethylbut-1-ene (18.8g.) in methylene chloride (35ml.) was added dropwise to a stirred solution of aluminium chloride (25.5g.) and dichlorophenylphosphine (33g.) in dry methylene chloride (120 ml.) at 0°C. The solution was stirred for a further 15 hours, followed by decomposition by dropwise addition to ice (1.5kg.). The organic layer was separated, dried, and the solvent removed, leaving an oil which crystallised on trituration with cold light petroleum. Recrystallisation from light petroleum gave 2,2,3,3-tetramethyl-1-phenylphosphetane-1-oxide (53%), m.p. 83 - 84°C, doublet at τ 9.07 (3H, J_{PH} = 20.0 c/sec), doublet at τ 8.62 (3H, J_{PH} = 17.5c/sec), singlet at τ 9.0 (3H), singlet at τ 8.62 (3H), multiplet at τ 6.9 - 7.92 (2H), and multiplet at τ 1.97 - 2.68 (5H). In benzene, singlet at τ 9.16 (3H), singlet at τ 8.77 (3H), doublet at τ 9.22 (3H, J_{PH} = 19.5c/sec) and doublet at τ 8.71 (3H, J_{PH} = 17.0 c/sec). ν max. 1178, 1153 and 1110cm.$^{-1}$.

Preparation of 2,2,3,3-Tetramethyl-1-phenylphosphetane.

This phosphetane was prepared in the same manner as 2,2,3-trimethyl-1-phenylphosphetane using triethylamine and trichlrosilane, b.p. 98 - 102°/0.5 m.m. 78% yield.

Reaction of 2,2,3,3-Tetramethyl-1-phenylphosphetane-1-oxide with sodium hydroxide.

The phosphetane oxide (0.75g.) in 2N sodium hydroxide solution (40ml.) and ethanol (10ml.) was refluxed for 48 hours. On dilution with cold water (100ml.), the alkaline solution was extracted with methylene chloride, which on work-up gave the starting material (400 mg.). The aqueous layer was acidified and extracted with methylene chloride until the aqueous layer was clear. The combined organic extracts were dried and the solvent removed, giving 1,1,2,2,-tetramethylpropylphenylphosphinic acid (44%) m.p. 169 - 171°C (from water), $^{m}/_{e}$ 480, 381, 362, 339, 317, 240, 225, 198, 184, 161 and 142. In

CCl_4, singlet at τ 9.05 (9H), doublet at τ 9.03 (6H, J_{PH} = 17c/sec.), multiplet at τ 2.08 - 2.82 (5H), and broad singlet at τ -2.45 (1H). $\nu_{max.}$ broad peaks at 2280 and 1740, 1468, 1181, 1120, 1070, 973 and 949 $cm.^{-1}$.

(Found: C, 63.74; H, 8.6; P, 13.2. $C_{13}H_{21}O_2P$ requires C, 65.0; H, 8.75; P, 12.92%).

Preparation of 1-Benzyl-2,2,3,3-Tetramethyl-1-phenylphosphetanium Bromide.

Quaternisation of the phosphetane with benzyl bromide in benzene at room temperature for 48 hours gave 1-benzyl-2,2,3,3-tetramethyl-1-phenylphosphetanium bromide (96%) m.p. 258 - 260°(from methylene chloride), $\nu_{max.}$ 1440, 1180, 1157, 1132, 1117 and 1067 $cm.^{-1}$.
(Found: C, 63.71; H, 6.64; P, 8.08. $C_{20}H_{26}BrP$ requires C, 63.66; H, 6.9; P, 8.22%).

Separation of optical enantiomorphs.

A slurry of silver D(-)dibenzoylhydrogen tartrate (10g.) in methanol (30ml.) was added to a stirred solution of the phosphetanium bromide (10g.) in methanol (100ml.). After 1 hour, the precipitate of silver bromide was filtered off and the solvent removed, leaving a white solid of 1-benzyl-2,2,3,3-tetramethyl-1-phenylphosphetanium D(-)dibenzoylhydrogen tartrate (98%) (from chloroform-ethyl acetate). The phosphetanium salt was fractionally recrystallised from n-propanol giving five fractions. The first two fractions had $(\alpha)_D^{MeOH}$ between -48.5° and 49.3° which were not changed by further recrystallisation. The third and fourth fractions had slightly lower optical rotations, whilst the fifth fraction, an oil, had $(\alpha)_D^{MeOH} = 29°$. The combined first and second fractions (1.85g.) after metathesis with ammonium iodide, and recrystallisation from chloroform-ethyl acetate gave 1-benzyl-2,2,3,3-tetramethyl-1-phenylphosphetanium iodide (89%), m.p. 263.5 - 264°, $(\alpha)_D^{MeOH} = +21.4°$ which after repeated recrystallisation reached + 21.8°.

589 + 21.8 578 + 22.2 546 + 25.5 436 + 44.2 365 + 45.5

The fifth fraction (4.7g.), after metathesis with ammonium iodide, gave the phosphetanium iodide (3.5g.), which on fractional crystallisation from chloroform-ethyl acetate gave the salt with partial optical activity (0.6 g.) $(\alpha)_D^{MeOH}$ - 9.4° (temp 11°C) and optically inactive salt (2.7 g.).

589 - 9.4° 578 - 10.0° 546 -11.0° 436 -17.5° 365 -25°

(Found: C, 57.1; H, 6.13; P, 6.8. $C_{20}H_{26}IP$ requires C, 56.6; H, 6.13; P, 7.3%).

Hydrolysis of 1-Benzyl-2,2,3,3-Tetramethyl-1-phenylphosphetanium Iodide.

A solution of the phosphetanium iodide (180mg.) $(\alpha)_D^{MeOH}$ + 21.8° in ethanol (10ml.) and 0.1 N sodium hydroxide solution (10ml.) was set aside at room temperature for 60 hours. The aqueous solution was extracted with chloroform which was dried and removed, leaving a crystalline solid (89 mg.), $(\alpha)_D^{MeOH}$ + 37.5°, (t = 10.5°C). Repeated recrystallisation from light petroleum gave (+) 2,2,3,3-tetramethyl-1-phenylphosphetane-1-oxide.

589 + 37.1° 578 + 37.1° 546 + 43.3° 436 + 84.0° 365 + 151.0° (t = 10.5° C)

Repeating the experiment with the phosphetanium iodide $(\alpha)_D^{MeOH}$ - 9.4° gave the corresponding phosphetane oxide $(\alpha)_D$ -15.4 (temp. 11.0°) after chromatography on alumina.

589 -15.4° 578 -15.2° 546 - 17.3° 436 -32.0° 365 -46.1°

Wittig Olefin Synthesis on 1-Benzyl-2,2,3,3 Tetramethyl-1-phenylphosphetanium Iodide

The phosphetanium iodide (0.25g.) $(\alpha)_D$ + 21.8° (methanol) was stirred with 1.8 N butyllithium (0.5ml.) in dry tetrahydrofuran (25ml.) at room temperature for $\frac{1}{4}$ hour. Benzaldehyde (0.5 ml.) was added and the solution was stirred for a further 6 hours. The solvent was removed and the residue in methylene chloride was washed, dried and the solvent again removed. The residue was chromatographed on basic alumina and

elution with ether-methanol (50:1) gave 2,2,3,3-tetramethyl-1-phenyl-phosphetane-1-oxide

589 + 36.6° 578 + 36.5° 546 41.7° 436 + 78.5° 365 + 155.0° in methanol, temp. = 14.25°C.

Repeating the experiment with the phosphetanium iodide $(\alpha)_D$ -9.4° (methanol) gave the corresponding phosphetane oxide $(\alpha)_D$ -15.2° (methanol) temp = 12.5°C.

589 -15.2° 578 -15.3° 546 -17.8° 436 -36.1° 365 -49.8°

Repeated recrystallisation of the oxide from light petroleum increased the optical rotation to -29° when lack of material prevented further progress.

Preparation of 2,2,3,4,4-Pentamethyl-1-phenylphosphetane-1-oxide m.p. 118°C.

2,4,4-Trimethylpent-2-ene (33.1g.) was added dropwise to a stirred solution of dichlorophenylphosphine (51.5g.) and aluminium chloride (40g.) in methylene chloride (150ml.) at 0°C. After stirring for a further 3 hours, the solution was added slowly dropwise to a slurry of ice-water (3kg.) over a period of 2½ hours. The organic layer was separated, dried, and the solvent removed. The oily residue (33g.) was chromatographed on basic alumina (900g.). Elution with petroleum spirit (40-60)-ether (1:1), (500ml.) gave the phosphetane oxide (3g.) m.p. 126°. Further elution with this eluent (5l.) and with ether (10l.) gave a mixture of the two geometrical isomers with ever increasing amount of the isomer m.p. 118°C. Elution with ether-methanol (100:1) (3.5 l.) gave pure 2,2,3,4,4-pentamethyl-1-phenylphosphetane-1-oxide (13g.), m.p. 118°C. In CCl_4, doublet at τ 8.70 (6H, J_{PH} = 20c/sec.), doublet at τ 8.8 (6H, J_{PH} = 19c/sec.), and doublet at τ 9.02 (3H, J_{HH} = 7.0c/sec.).

Reduction of 2,2,3,4,4-Pentamethyl-1-phenylphosphetane-1-oxide, (m.p. 118°C).

A solution of the oxide (7.08 g.) and trichlorosilane (8.2 g.) in methylene chloride (50ml.) was stirred at 0°C for three hours until hydrogen evolution ceased. Excess benzyl bromide was added and the solution was stirred for a further 24 hours at 0°C. Water was then added and silica was filtered off. The filtrate was dried, the solvent removed and the residue recrystallised from chloroform-ethyl acetate, giving 1-benzyl-2,2,3,4,4,-pentamethyl-1-phenylphosphetanium bromide (92%) consisting of 90% from the oxide m.p. 118°C and 10% from the oxide m.p. 126°C.

Hydrolysis of 1-Benzyl-2,2,3,4,4-Pentamethyl-1-phenylphosphetanium Bromide.

The phosphetanium salt (200mg.) of both 90:10 and 72:28 isomer ratio '118:126' was hydrolysed in aqueous alkali having normalities 0.02N, 0.1N, N and 5N. In each case the 2,2,3,4,4-pentamethyl-1-phenylphosphetane-1-oxide had isomer ratio 9:91:: '118:126' in yields of 94 - 97%.

The isomers were not interconvertible under any alkaline or acid conditions, and were completely stable to alkali, even 10N, NaOH at 100°C for two days.

Hydrolysis of 1-Benzyl-2,2,3,4,4-Pentamethyl-1-phenylphosphetanium Bromide in D_2O/NaOD.

A solution of the phosphetanium salt (72:28::118:126) (470mg.) in 1N sodium deuteroxide (5ml.) in deuterium oxide (10ml.) was set aside at room temperature for 18 hours. The solution was extracted with methylene chloride, which was then dried, and the solvent removed. The crystalline residue of 2,2,3,4,4-pentamethyl-1-phenylphosphetane-1-oxide (97%) with isomer ratio of 91:9::126:118 showed no incorporation of deuterium anywhere in the molecule.

Experiment to Test the Stability of 1-Benzylidene-2,2,3,4,4 Pentamethyl-1-phenyl-phosphetane.

The phosphetanium salt (1.0g.) (90:10::118:126) was stirred with 1.8N butyllithium (1.5 ml.) in dry tetrahydrofuran (75ml.) at room temperature for 75 minutes.

(a) Half the solution (37 ml.) was then added to 66% hydriodic acid (20ml.). This solution was diluted with water (100ml.) and was extracted with methylene chloride until no further colouration was present in the organic layer. The combined organic fractions were dried, the solvent removed and the residue triturated with ether (300ml). The red coloured residue insoluble in ether was recrystallised from chloroform-ethyl acetate yielding 1-benzyl-2,2,3,4,4-pentamethyl-1-phenylphosphetanium iodide (or periodide) (190mg.). ^{1}H N.M.R. showed that the isomer ratio had changed to 45:55::118:126.

(b) The remaining half of the ylid solution was treated with benzaldehyde (0.8g.) and was stirred for 18 hours. The solvent was removed and the residue in methylene chloride was washed with water, dried, and the solvent again removed. The residue was chromatographed on basic alumina (30g.). Elution with ether-methanol (50:1) gave 2,2,3,4,4-pentamethyl-1-phenylphosphetane-1-oxide (93%) having isomer ratio 43:57::118:126.

When the benzylidene ylid solution was set aside for 18 hours and then worked up in the same ways, treatment of the ylid with HI gave the phosphetanium salt (16%) with isomer ratio 41:59::118:126. Treatment of the ylid with benzaldehyde gave the phosphetane oxide with isomer ratio 38:62::118:126.

Reaction of 2,2,3,4,4-Pentamethyl-1-phenylphosphetane with 9,10 Phenanthraquinone.

Equimolar quantities of the phosphetane and 9,10-phenanthraquinone were mixed in a flask at 0°C. After an exothermic reaction trituration with ethyl acetate gave orange yellow crystals of the 1:1 adduct, m.p. 198-199° C.(from ethyl acetate). ^{1}H N.M.R. in

o-dichlorobenzene, doublet at τ 8.47 (6H, J_{PH} = 16c/sec.), doublet at τ 8.64 (6H, J_{PH} = 19c/sec.) and quartet at τ 9.18 (3H, J_{PH} = 1.0c/sec., J_{HH} = 7c/sec.). ^{31}P N.M.R. (C_6H_6) at -0.5 p.p.m. (85% H_3PO_4), $^m/e$ 428, 358, 343, 315, and 239. $\nu_{max.}$ 1640, 1340, 1119, 1110, 1055, 1030 and 930 $cm.^{-1}$.

(Found: C, 78.15; H, 6.78; P, 7.60. $C_{28}H_{29}O_2P$ requires C, 78.5; H, 6.77; P, 7.24%).

Reaction of 2,2,3,4,4-Pentamethyl-1-phenylphosphetane with Dimethylacetylene dicarboxylate.

Dimethyl acetylene dicarboxylate (1.3g.) in dry benzene was added dropwise to a solution of the phosphetane (1.0 g.) in benzene (20ml.) at 0°C. After an exothermic reaction, the solvent was removed and the red coloured residue was triturated with ether to give an oily solid whose I.R. and N.M.R. spectra showed very broad, ill defined peaks. This material was chromatographed on silica and on elution with eluents of greater polarity than ether-petrol (1:3) gave a red oil whose ^1H N.M.R. showed broad peaks, $\nu_{max.}$ 1720, 1440, 1215, 1200, 1162, 1012 and 992 $cm.^{-1}$.

Elution with ether gave a white crystalline solid (240mg.), m.p. 155 - 155.5°C (purified by sublimation), $^m/e$ 410, 378, 237, 218 and 146, singlet at τ 5.68 (3H) and multiplet at τ 6.0 - 6.15 (15H). $\nu_{max.}$ 1736, 1728, 1610, 1434, 1318, 1253, 1228, 1208, 1180, 1110, 998 and 980 $cm.^{-1}$.

(Found: C, 52.59; H, 4.5; $C_{18}H_{18}O_{11}$ requires C, 52.68; H, 4.29%). This compound was unaffected by hydrogenation with a palladium-charcoal catalyst and by treatment with bromine in carbon tetrachloride.

REFERENCES.

1. G. Wittig and U. Schöllkopf, Chem. Ber., 1954, 87, 1318
2. H. Staudinger and J. Meyer, Helv. Chim. Acto, 1919, 2, 635.
3. G.I. Derkach and A.V. Kirsanov, Zhur. Obsh. Khim., 1958, 28, 1887. 1959, 29, 3424.
4. A.J. Speziale and D.E. Bissing, J. Amer. Chem. Soc., 1963, 85, 1888.
5. L.D. Bergelson and M.M. Shemyakin, Tetrahedron, 1963, 19, 149
6. L.D. Bergelson, L.I. Barsukov and M.M. Shemyakin, Tetrahedron, 1967, 23, 2709.
7. M. Schlosser and K.F. Christmann, Annalen, 1967, 708, 1.
8. C.A. VanderWerf, A. Bladé-Font and W.E. McEwen, J. Amer. Chem. Soc., 1960, 82, 2396.
9. R.F. Hudson, "Structure and Mechanism in Organophosphorus Chemistry", Academic Press, New York, 1965.
10. A.W. Johnson, "Ylid Chemistry", Academic Press, New York, 1966.
11. A.J. Kirby and S.G. Warren, "The Organic Chemistry of Phosphorus", Elsevier, Amsterdam, 1967.
12. A. Maercker, "Organic Reactions, Vol. 14, J. Wiley and Sons, New York, 1965.
13. S. Trippett, Quarterly Rev., 1963, 17, 406.
14. G. Wittig, Angew. Chem., 1956, 68, 505.
15. A.W. Hofmann, Annalen Suppl., 1861, 1, 145, 275.
16. M. Grayson, P.T. Keough and M.E. Rauhut, U.S. 3,214,434; C.A., 1966, 64, 15924.
17. P.T. Keough and M. Grayson, J. Org. Chem., 1964, 29, 631.
18. D. Seyferth and J. Fogel, J. Organometal. Chem., 1966, 6, 205.
19. G. Wittig, H. Eggers and P. Duffner, Annalen, 1958, 619, 10.
20. E.E. Schweizer and R.D. Bach, J. Org. Chem., 1964, 29, 1746.
21. E. Zbiral and E. Werner, Annalen, 1967, 707, 130.
22. G. Pattenden and B.J. Walker, J. Chem. Soc. C, 1969, 531.

23. H. Hoffmann and M. Beller, unpublished results. Quoted by H. Hoffmann, Angen. Chem., 1964, 76, 944.

24. L. Horner, G. Mummenthy, H. Moser and P. Beck, Chem. Ber., 1966, 99, 2782.

25. J.J. Brophy, K.L. Freeman and M.J. Gallagher, J. Chem. Soc. C, 1968, 2760.

26. H. Hoffmann and H-J. Diehr, Chem. Ber., 1965, 98, 363.

27. M.P. Savage and S. Trippett, J. Chem. Soc. C, 1968, 591.

28. A.M. Aguiar and D. Diagle, J. Amer. Chem. Soc., 1964, 86, 2299; J. Org. Chem., 1965, 30, 2826; J. Org. Chem., 1965, 30, 3527.

29. A.M. Aguiar and T.G. Archibald, Tetrahedron Letters, 1966, 5471, 5541.
A.M. Aguiar, T.G. Archibald and L.I. Kapicak, Tetrahedron Letters, 1967, 4447.

30. A.M. Aguiar and H. Aguiar, J. Amer. Chem. Soc., 1966, 88, 4090.

31. E. Zbiral and L. Berner-Fenz, Tetrahedron, 1968, 24, 1363.

32. E. Zbiral and L. Berner-Fenz, Monatsch. Chem., 1967, 98, 666.

33. H.C. Gilman and R.A. Tomasi, J. Org. Chem., 1962, 27, 3647.

34. G.H. Birum and C.N. Matthews, Chem. Comm., 1967, 137.

35. R.N. Ring, G.C. Tesoro and D.R. Moore, J. Org. Chem., 1967, 32, 1091.

36. E.E. Schweizer, J. Amer. Chem. Soc., 1964, 86, 2744.

37. E.E. Schweizer and K. Light, J. Org. Chem., 1966, 31, 870.

38. E.E. Schweizer and L.D. Smucker, J. Org. Chem., 1966, 31, 3147.

39. E.E. Schweizer, J. Liehr and D.J. Monaco, J. Org. Chem., 1968, 33, 2416.

40. E.E. Schweizer, L.D. Smucker and R. Votral, J. Org. Chem., 1966, 31, 467.

41. W.M. Daniewski and C.E. Griffin, J. Org. Chem., 1966, 31, 3236.

42. N. Takashina and C.C. Price, J. Amer. Chem. Soc., 1962, 84, 489.

43. G. Kamai and V.A. Kuhktin, Zh. Obsh. Khim. SSSR, 1957, 27, 2431.

44. H. Hoffmann, Chem. Ber., 1961, 94, 1331.

45. R.G. Harvey, Tetrahedron, 1966, 22, 2561.

46. W.H. Dietsche, Tetrahedron Letters, 1966, 6347.

47. R. Oda, T. Kawabata and S. Tanimoto, Tetrahedron Letters, 1964, 1653.

48. S. Trippett, Chem. Comm., 1966, 468.

49. K.D. Berlin and G.B. Butler, J. Org. Chem., 1961, 26, 2537.

50. F.G. Mann, I.T. Millar and F.H.C. Stewart, J. Chem. Soc., 1954, 2832.

51. A.E. Arbusov and K.V. Nikonorov, Zh. Obsh. Khim., 1948, 18, 2008.

52. R.W. Turner and A.H. Soloway, J. Org. Chem., 1965, 30, 4031.

53. L. Horner and W. Hofer, Tetrahedron Letters, 1966, 3321.

54. S. Trippett, Private Communication.

55. H. Suzuki, Bull. Chem. Soc. Japan, 1952, 25, 145.

56. J. Meisenheimer, J. Casper, M. Höring, W. Lauter, L. Lichtenstadt, and W. Samuel, Annalen, 1926, 449, 213.

57. M. Zanger, C.A. VanderWerf and W.E. McEwen, J. Amer. Chem. Soc., 1959, 81, 3806.

58. G. Aksnes and K. Bergesen, Acta Chem. Scand., 1965, 19, 931.

59. G.W. Fenton and C.K. Ingold, J. Chem. Soc., 1929, 2342.

60. L. Horner, H. Hoffmann, H.G. Wippel and G. Hassel, Chem. Ber., 1958, 91, 52.

61. J.J. Brophy and M.J. Gallagher, Chem. Comm., 1967, 344.

62. G. Aksnes, Acta Chem. Scand., 1961, 15, 438.

63. A.R. Hands and A.J.H. Mercer, J. Chem. Soc., 1965, 6055.

64. M.J. Gallagher and I.D. Jenkins, "Stereochemical Aspects of Phosphorus Chemistry" in "Topics in Stereochemistry" Vol. 3, ed. E.L. Eliel and N.L. Allinger. W.J. Wiley, New York, 1968.

65. J.J. McBride, E. Jungermann, J.V. Killheffer and R.J. Clutter, J. Org. Chem., 1962, 27, 1833.

J.J. McBride, E. Jungermann, R.J. Clutter and A. Mais, J. Org. Chem., 1962, 27, 606.

66. W. Hawes, Ph.D. Thesis, University of Leicester, 1968.

67. S.E. Fishwick, J. Flint, W. Hawes and S. Trippett, Chem. Comm., 1967, 1113.

68. S.E. Cremer and R.J. Chorvat, J. Org. Chem., 1967, 32, 4066.

69. S.E. Cremer, R.J. Chorvat, C.H. Chang and D.W. Davis, Tetrahedron Letters, 1968, 5796.

70. W.R. Vaughan, R.S. Klonowski, B.B. Millward and R.S. McElhinney, J. Org. Chem., 1961, 26, 138.

71. V.R. Gaertner, Tetrahedron Letters, 1966, 4691.

72. B.J. Gaj and D.R. Moore, Tetrahedron Letters, 1967, 2155.

73. D. Berglund and D.W. Meek, J. Amer. Chem. Soc., 1968, 90, 519.

74. A.R. Panteleeva and I.M. Shermergorn, Izv. Akad. Nauk. SSSR., Sehr. Khim., 1968, 1652 (E).

75. R.I. Wagner, U.S. 3,086,053; C.A. 1963, 59, 10124.

76. G.M. Kosolapoff and R.F. Struck, J. Chem. Soc., 1957, 3739.

77. S.O. Grim and R. Schaaff, Angew. Chem. Internat. Ed., 1963, 2, 486.

78. S.A. Buckler and V.P. Wystrach, J. Amer. Chem. Soc., 1961, 83, 168.

79. M. Green, J. Chem. Soc., 1965, 541.

80. L.D. Quin and D.A. Mathewes, J. Org. Chem., 1964, 29, 836.

81. W.B. McCormack, U.S. 2,663,736 and U.S. 2,663,737.

82. A. Michaelis and H. v. Soden, Annalen, 1885, 229, 295.
A. Michaelis, Annalen, 1901, 315, 43.

83. G. Aksnes and J. Songstad, Acta Chem. Scand., 1962, 16, 1426.

84. H. Hoffmann, Annalen, 1960, 634, 1.

85. W.E. McEwen, G. Axelrad, M. Zanger and C.A. VanderWerf, J. Amer. Chem. Soc., 1965, 87, 3948.

86. G. Aksnes and L.J. Brudvik, Acta Chem. Scand., 1963, 17, 1616.

87. K. Bergesen, Acta Chem. Scand., 1966, 20, 899.

88. W.E. McEwen, "Topics in Phosphorus Chemistry", Vol. 2., Interscience, New York, 1965.

89. G. Wittig, Bull. Soc. Chim. France, 1966, 1162.

90. W.E. McEwen, K.F. Kumli and C.A. VanderWerf, J. Amer. Chem. Soc., 1959, 81, 3805.

91. L. Horner and H. Winkler, Tetrahedron Letters, 1964, 3265.

92. L. Horner and H. Winkler, Tetrahedron Letters, 1964, 175.

93. L. Horner, H. Winkler, A. Rapp, A. Mentrup, H. Hoffmann and P. Beck, Tetrahedron Letters, 1961, 161.

94. W.E. McEwen, K.F. Kumli, A. Bladé-Font, M. Zanger and C.A. VanderWerf, J. Amer. Chem. Soc., 1964, 86, 2378.

95. D.E.C. Corbridge,"Topics in Phosphorus Chemistry", Vol. 3, Interscience, New York, 1966.

96. S. Trippett, Leicester Chem. Rev., 1969, 10, 40.

97. C. Chioccola and J.J. Daly, J. Chem. Soc. A, 1968, 568.

98. P.J. Wheatley, J. Chem. Soc., 1964, 2206.

99. F. Ramirez, A.J. Bigler and C.P. Smith, J. Amer. Chem. Soc., 1968, 90, 3507.

100. R. D. Spratley, W.C. Hamilton and J. Lodell, J. Amer. Chem. Soc., 1967, 89, 2272.
W.C. Hamilton, S.J. LaPlaca, F. Ramirez and C.P. Smith, J. Amer. Chem. Soc., 1967, 89, 2268.
W.C. Hamilton, S.J. LaPlaca and F. Ramirez, J. Amer. Chem. Soc., 1965, 87, 127.

101. D. Hellwinkel, Chem. Ber., 1966, 99, 3628.

102. E.L. Muetterties and R.A. Schunn, Quarterly Rev., 1966, 20, 245.

103. R.S. Berry, J. Chem. Phys., 1960, 32, 933.

104. E.L. Muetterties, Inorg. Chem., 1967, 6, 635.

105. M. Green and R.F. Hudson, J. Chem. Soc., 1963, 540.

106. R.U. Pagilagan and W.E. McEwen, Chem. Comm., 1966, 652.

107. L. Horner, H. Fuchs, H. Winkler and A. Rapp, Tetrahedron Letters, 1963, 965.

108. W. Hawes and S. Trippett, Chem. Comm., 1968, 295.

109. C.N. Caughlan and Mazhar-Ul-Haque, Chem. Comm., 1968, 1228.

110. H. Fritzsche, U. Hasserodt and F. Korte, Chem. Ber., 1965, 98, 171.

111. H. Fritzsche, U. Hasserodt and F. Korte, Ger. 1,203,773; Chem. Abs., 1966, 64, 3601.

112. L. Horner and H. Winkler, Tetrahedron Letters, 1964, 461.

113. C. Moret and L.M. Trefonas, J. Amer. Chem. Soc., 1969, 91, 2255.

114. D.D. Swank and C.N. Caughlan, Chem. Comm., 1968, 1051.

115. L. Horner and W. Balzer, Tetrahedron Letters, 1965, 1157.

116. L. Horner and H. Hoffmann, Chem. Ber., 1958, 91, 45.

117. J. Flint, Private Communication.

118. K.F. Kumli, W.E. McEwen and C.A. VanderWerf, J. Amer. Chem. Soc., 1959, 81, 248.

119. W.E. McEwen, D.M. Coyne and C.A. VanderWerf, J. Amer. Chem. Soc., 1956, 78, 3061.

120. K.L. Marsi, Chem. Comm., 1968, 846.

121. N.J. De'Ath and S. Trippett, Chem. Comm., 1969, 172.

122. R.F. Hudson, Angew. Chem. Internat. Ed., 1967, 6, 749.

123. E.A. Dennis and F.H. Westheimer, J. Amer. Chem. Soc., 1966, 88, 3432.

124. W. Hawes and S. Trippett, Chem. Comm., 1968, 577.

125. G. Aksnes and K. Bergesen, Acta Chem. Scand., 1966, 20, 2508.

126. R. Kluger, F. Kerst, D.G. Lee, E.A. Dennis and F.H. Westheimer, J. Amer. Chem. Soc., 1967, 89, 3918, 3919.

127. R. Greenhalgh and R.F. Hudson, Chem. Comm., 1968, 1300.

128. R.F. Hudson, R. Greenhalgh and R. Woodcock, Chem. Comm., 1968, 22.

129. K. Dimroth, K. Vogel, W. Mach and U. Schoeler, Angew. Chem. Int. Ed 1968, 7, 371.

130. P. Haake and P.S. Ossip, Tetrahedron, 1968, 24, 565.

131. S.E. Fishwick and J.A. Flint, Chem. Comm., 1968, 182.

132. H. Hellmann and J. Bader, Tetrahedron Letters, 1961, 724.

133. M. Schlosser, Angew. Chem., 1962, 74, 291.

134. D.W. Allen and I.T. Millar, Chem. and Ind. (London), 1967, 52, 2178.

135. D.W. Allen and I.T. Millar, J. Chem. Soc. C, 1969, 252.

136. E.M. Richards and J.C. Tebby, Chem. Comm., 1967, 957.

137. L.S. Bartell and K.W. Hansen, Inorg. Chem., 1965, 4, 1777.

138. G.H. Birum and C.N. Matthews, J. Org. Chem., 1967, 32, 3554.

139. E.L. Muetterties, W. Mahler and R. Schmutzler, Inorg. Chem., 1963, 2, 613.

140. E.L. Muetterties, W. Mahler, K.J. Packer and R. Schmutzler, Inorg. Chem., 1964, 3, 1298.

141. E.A. Dennis and F.H. Westheimer, J. Amer. Chem. Soc., 1966, 88, 3431.

142. F. Ramirez and N.B. Desai, J. Amer. Chem. Soc., 1963, 85, 3252.

143. V.A. Kukhtin and K.M. Kirillova, Zhur. Obsh. Khim. SSSR., 1962, 32, 2755.

144. D. Swank, C.N. Caughlan, F. Ramirez, O.P. Madan and C.P. Smith, J. Amer. Chem. Soc., 1967, 89, 6503.

145. F. Ramirez, C.P. Smith, A.S. Gulati and A.V. Patwardhan, Tetrahedron Letters, 1966, 2151.

146. L.I. Mizrah, L. Yu. Sandalova and V.P. Evdakov, Zh. Obsh. Khim., 1967, 37, 1786.

147. F. Ramirez, A.V. Patwardhan, and C.P. Smith, J. Amer. Chem. Soc., 1965, 87, 4973.

148. R. Burgada, Compt. Rend. Acad. Sci. Paris, C, 1964, 258, 4789.

149. F.Ramirez, A.V. Patwardhan, H.J. Kugler and C.P. Smith, Tetrahedron, 1968, 24, 2275.

150. F. Ramirez, A.V. Patwardhan, H.J. Kugler and C.P. Smith, Tetrahedron Letters, 1966, 3053.

151. L. Yu. Sandalova, L.I. Mizrah and V.P. Evdakov, Zh. Obsh. Khim., 1966, 36, 1451.

152. F. Ramirez, A.V. Patwardhan, H.J. Kugler and C.P. Smith, J. Amer. Chem. Soc., 1967, 89, 6276.

153. B.A. Arbusov, N.A. Polezhaëva and V.S. Vinogradova, Izvest. Akad. Nauk. S.S.S.R., 1967, 2281; C.A., 68, 69079.

154. D.G. Gorenstein and F.H. Westheimer, J. Amer. Chem. Soc., 1967, 89, 2762.

155. F. Ramirez, J.F. Pilot and C.P. Smith, Tetrahedron, 1968, 24, 3735.

156. F. Ramirez, J.F. Pilot, O.P. Maden and C.P. Smith, J. Amer. Chem. Soc., 1968, 90, 1275.

157. F. Ramirez, O.P. Maden and S.R. Heller, J. Amer. Chem. Soc., 1965, 87, 731.

158. H-J. Bestmann, Th. Denzel and R. Kunstmann, Tetrahedron Letters, 1968, 2895.

159. H-J. Bestmann and R. Kunstmann, Chem. Ber., 1969, 102, 1816.

160. L.V. Nesterov, R.A. Sabirova, N.E. Krepysheva and R.I. Mutalapova, Dokl. Akad. Nauk. S.S.S.R., 148, 1085, 1963; C.A. 59, 3757.

161. R. Burgada, D. Houalla and R. Wolf, Compt. Rend. Acad. Sci. Paris, C, 1967, 264, 356.

162. T. Reetz and J.F. Powers, U.S. 3,172,903; Chem. Abs. 63, 2981.

163. M. Sanchez, R. Wolf, R. Burgada and F. Mathis, Bull. Soc. Chim. France, 1968, 773.

164. F. Ramirez, A.J. Bigler and C.P. Smith, Tetrahedron, 1968, 24, 5041

165. N.A. Razumova and A.A. Petrov, Zh. Obsh. Khim., 1963, 33, 3796. Chem. Abs., 60, 10711.

166. N. Sanchez, J-F. Brazier, D. Houalla and R. Wolf, Bull. Soc. Chim. France, 1967, 3930.

167. H.R. Allcock and R.L. Kugel, Chem. Comm., 1968, 1606.

168. S. Trippett, J. Chem. Soc., 1962, 4731.

169. A.C. Chapman, W.S. Holmes, N.L. Paddock and H.T. Searle, J. Chem. Soc., 1961, 1825.

170. H. Hess and D. Forst, Z. anorg. allg. Chem., 1966, 342, 240.

171. M. Becke-Göhring, H-J. Wald and H. Weber, Naturwissenschaften, 1968, 55, 491.

172. F. Ramirez, C.P. Smith and J.F. Pilot, J. Amer. Chem. Soc., 1968, 90, 6726.

173. V. Prelog and J.A. Dunitz, Angew. Chem. Internat. Ed., 1968, 7, 725.

174. R.R. Holmes and R.M. Dieters, J. Amer. Chem. Soc., 1968, 90, 5021.

175. P.C. Lauterbur and F. Ramirez, J. Amer. Chem. Soc., 1968, 90, 6722.

176. H.S. Gutowsky, D.W. McCall and C.P. Slichter, J. Chem. Phys., 1953, 21, 279.

177. R. Schmutzler, Angew. Chem. Internat. Ed., 1965, 4, 496.

178. S.C. Peake and R. Schmutzler, Chem. Comm., 1968, 1662.

179. P.C. Van der Voorn and R.S. Drago, J. Amer. Chem. Soc., 1966, 88, 3255.

180. R.J. Gillespie, Can. J. Chem., 1960, 38, 818; 1961, 39, 318; J. Chem. Soc., 1963, 4672.

181. F. Ramirez, Accounts Chem. Res., 1968, 1, 168.

182. V.A. Kukhtin, K.M. Kirillova, R.R. Shagidullin, Yu.Yu. Samitov, N.A. Lyazina and F.N. Rakova, Zh. Obsh. Khim., 1962, 32, 2039.

183. P.C. Haake and F.H. Westheimer, J. Amer. Chem. Soc., 1961, 83, 1102.

184. D.A. Usher, E.A. Dennis and F.H. Westheimer, J. Amer. Chem. Soc., 1965, 87, 2320.

185. D. Gorenstein and F.H. Westheimer, Proc. Nat. Acad. Sci. U.S., 1967, 58, 1747.

186. F.H. Westheimer, Accounts Chem. Res., 1968, 1, 70.

187. D. Houalla, R. Wolf, D. Gagnaire and J.B. Robert, Chem. Comm., 1969, 443.

188. D. Hellwinkel, Angew. Chem. Internat. Ed., 1965, 4, 356.

189. D. Hellwinkel, Angew. Chem. Internat. Ed., 1966, 5, 725.

190. G.M. Whitesides and W.M. Bunting, J. Amer. Chem. Soc., 1967, 89, 6801.

191. D. Hellwinkel, Chimia, 1968, 22, 488.

192. D.S. Frank and D.A. Usher, J. Amer. Chem. Soc., 1907, 89, 6360.

193. F. Ramirez, A.S. Gulati and C.P. Smith, Unpublished results quoted in reference 181.

194. A.N. Hughes and S. Uaboonkul, Tetrahedron, 1968, 24, 3437.

195. J.C. Tebby, Private Communication.

196. N.E. Waite, J.C. Tebby, R.S. Ward and D.H. Williams, J. Chem. Soc. C., 1969, 1100.

197. A.W. Johnson and J.C. Tebby, J. Chem. Soc., 1961, 2126.

198. P.T. Keough and M. Grayson, J. Org. Chem., 1962, 27, 1817.

199. A. Michaelis and E. Gleichmann, Chem. Ber., 1882, 15, 801.

200. A. Klages and F. Tetzner, Chem. Ber., 1902, 35, 3967.

201. K. Auwers and A. Fruhling, Annalen, 1921, 422, 221.

202. S. Trippett and B.J. Walker, J. Chem. Soc. C, 1966, 887.

203. B.A. Arbusov and N.P. Grechkin, Zhur. Obsh. Khim., 1950, 20, 107.

204. M.P. Savage, Ph.D. Thesis, University of Leicester, 1967.

205. J. Sauvage, Compt. Rend. Acad. Sci. Paris, 1904, 139, 674.

206. P. Pfeiffer, I. Heller and H. Pietsch, Chem. Ber., 1904, 37, 4620.