SOME REACTIONS OF PHOSPHORUS HETEROCYCLES

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by

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To Jane

ABSTRACT

SOME REACTIONS OF PHOSPHOROUS HETEROCYCLES

C. M. BROWN

The preparation of phosphoranes and their uses in the synthesis of non-phosphorus containing molecules are reviewed. The photolysis and vacuum flash thermolysis (V.F.T.) of two new oxazaphospholans, 5,9-diphenyl-2,3-benzo-9-aza-1,4,6-trioxa-5-phosphaspiro-[4,4]-nonane and 9-methyl-5-phenyl-2,3-benzo-9-aza-1,4,6-trioxa-5-phosphaspiro-[4,4]-nonane are outlined. The V.F.T. and photolysis of some 1,3,2-dioxaphospholans are also mentioned.

A review of phenylphosphinidene, phenylphosphinothioylidene and phenylphosphinylidene is given. 2,3-Diphenyl-1,3,2-oxazaphospholene is investigated as a possible precursor to phenylphosphinylidene. The results of a number of attempted trapping reactions upon this species are discussed.

The photolysis of 1,2-dihydronaphthalenes, chromenes, isochromenes, thiochromenes and related compounds is reviewed. Work showing that the photolysis of 1-substituted-dihydrophosphinoline oxides gives similar products is included. The syntheses of phosphorinans, phosphorindienes, phosphinolines and isophosphinolines are discussed. The products obtained from the photolysis of a number of new 1-substituted-(1,2)-dihydrophosphinoline oxides are identified. Attempts to trap out the intermediate species in these reactions with other trapping reagents although unsuccessful are discussed.

A short review is given of monometaphosphate and similar species. Finally preparations of 1,2-oxaphosphol-3-ene 2-oxides are reviewed and the reactions of some of them outlined.

ACKNOWLEDGEMENTS

I wish to thank my supervisor, Dr. D. J. H. Smith, for his inspiration, encouragement and guidance at all stages of this work.

I would also like to thank Dr. Neil Hales and other members of the DJHS group for many valuable discussions related to the work. I am extremely grateful to the technical assistants in this Department for recording the mass spectra and ^{31}P n.m.r. spectra of my compounds. I would also like to thank Mrs. C. A. Crane for drawing the figures and Miss V. Orson-Wright for typing the thesis.

Thanks to the many friends who made my time at Leicester pass so quickly especially Robin Waddling, Matthew Walker and Mike Webb.

Finally, I should like to thank my wife and parents for their constant support and for putting up with me during the writing of this thesis and the Science Research Council for a maintenance grant.

STATEMENT

This thesis is based on work conducted by myself in the Department of Chemistry of the University of Leicester mainly during the period between October 1975 and October 1978.

All the work recorded in this thesis is original unless otherwise acknowledged in the text or by references. None of the work has been submitted for another degree in this or any other University.

C. M. BROWN

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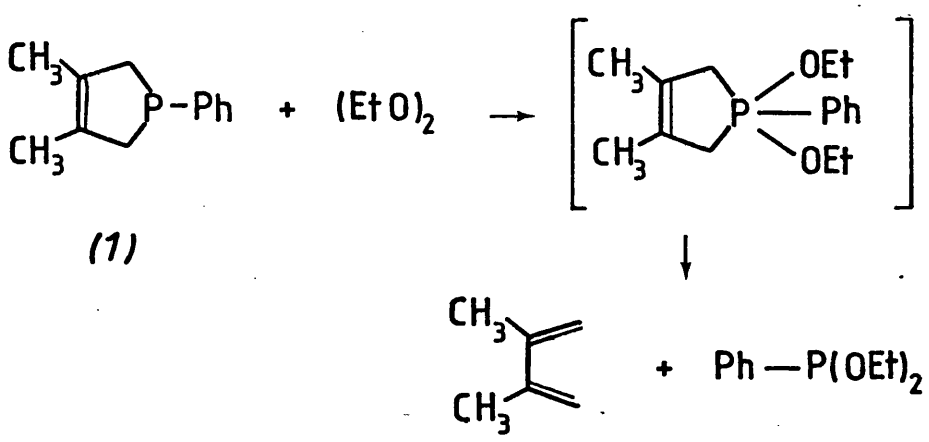
CHAPTER ONE

CHAPTER ONE

THE USE OF PHOSPHORANES IN SYNTHESIS

Phosphoranes are compounds in which the central phosphorus atom is surrounded covalently by five ligands. A large number of reactions have been reported in the literature in which phosphoranes have been used or postulated as intermediates in, the preparation of non-phosphorus containing compounds.

Denney [1] has shown that when 3,4-dimethyl-1-phenylphospho1-3-ene *(1)* is allowed to react with diethyl peroxide a phosphorane is formed which decomposes at room temperature.

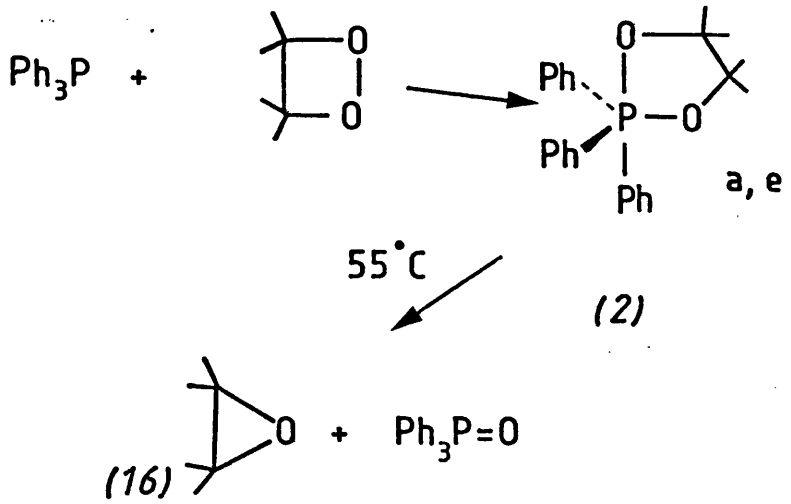


(1)

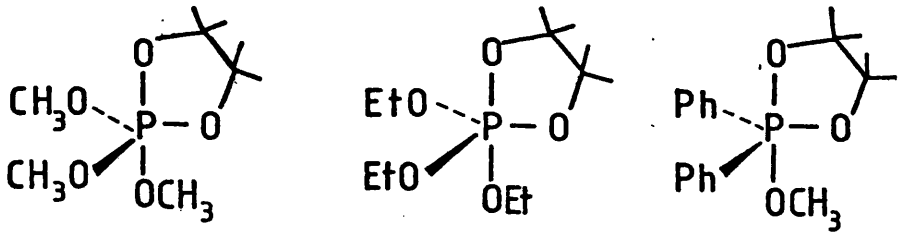
The products formed are 2,3-dimethylbuta-1,3-diene and diethyl phenyl-phosphonite. The ^{31}P n.m.r. spectrum shows no sign of the pentavalent phosphorus intermediate but its intermediacy was assumed from the products obtained. Since 1,2-dioxetane undergoes a similar reaction with the phosphine *(1)*, the authors suggest that the reaction cannot proceed <u>via</u> a transition state in which the two oxygen atoms occupy apical positions, as this ring cannot span such a distance.

Bartlett [2] reported the quantitative formation of the phosphorane

(2) in the reaction of 3,3,4,4-tetramethyl-1,2-dioxetane with triphenylphosphine. At 55°C, *(2)* smoothly decomposes to triphenylphosphine oxide and tetramethylethylene oxide *(16)*.



Subsequently, the preparation of three more phosphoranes by this method *(3,4,5)* was reported [3]. Unlike the phosphorane *(2)*, these were found to be thermally stable in benzene at 70°C for 120 minutes. In fact *(3)* could be heated in benzene (sealed tube) at 90°C for 12 hours with only slight decomposition taking place. These results were rationalized as showing the increased stability of the phosphoranes *(3,4,5)* by replacing the apical aryl group of *(2)* with an alkoxy group.

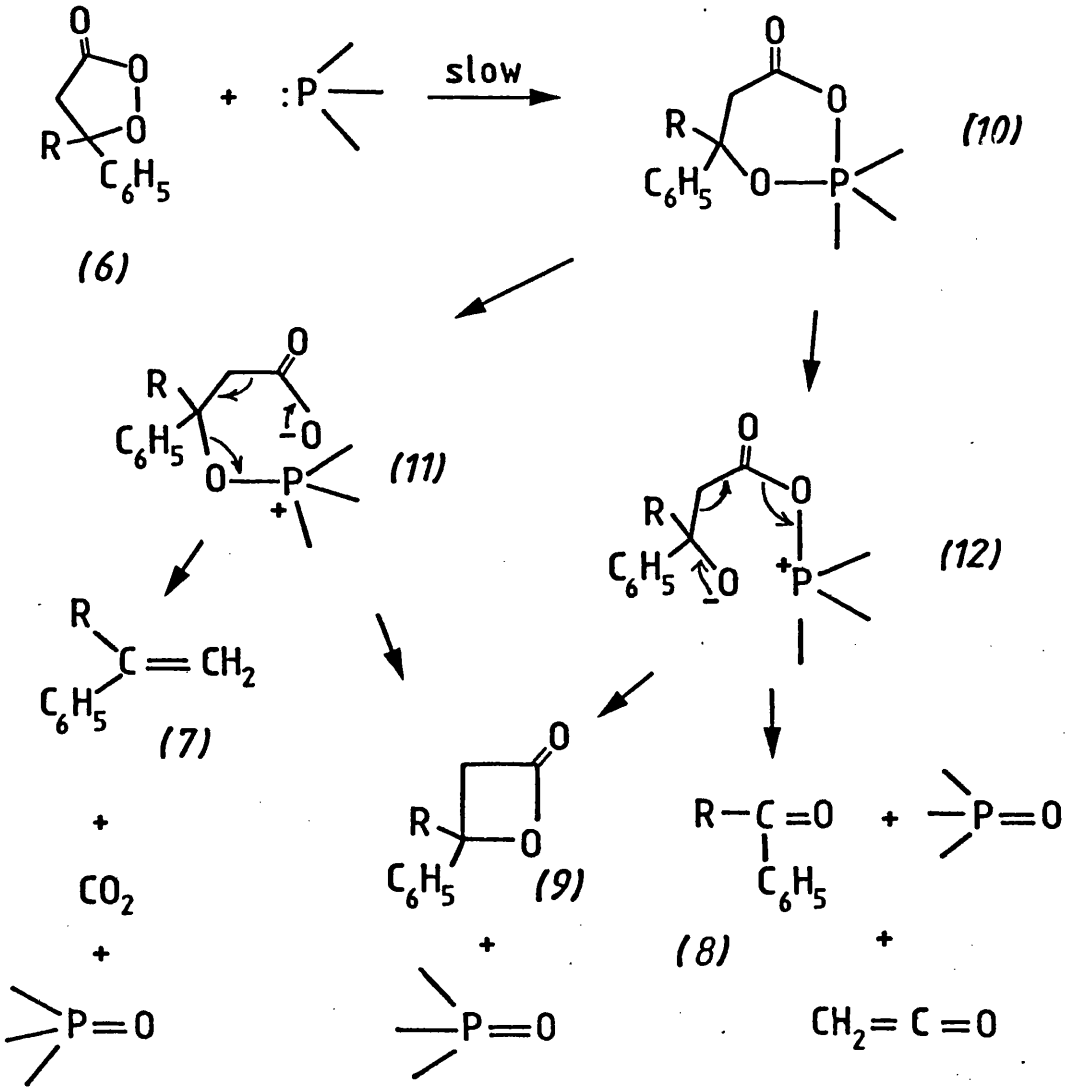


(3) *(4)* *(5)*

There are negligible solvent effects in the reaction of trivalent phosphorus compounds and 3,3,4,4-tetramethyl-1,2-dioxetane thus indicating the absence of a polar transition state. The reaction must

therefore be either concerted or homolytic in character.

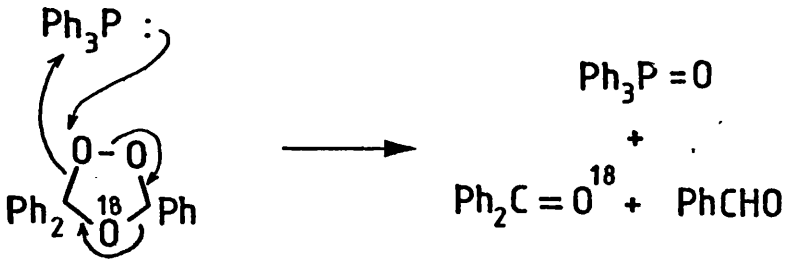
Work by Adam [4] has shown that the treatment of the peroxy compound *(6)* with triphenylphosphine in n-hexane at room temperature leads to quantitative precipitation of triphenylphosphine oxide and evolution of a gas. The products identified in the reaction mixture included an α-alkylstyrene *(7)*, an alkyl phenyl ketone *(8)* and small amounts of the lactones *(9)* (Scheme 1). The formation of the ketone requires that ketene is also produced and present in the gas evolved along with carbon dioxide.



SCHEME 1

The authors trapped the ketene with menthol, benzyl alcohol, and phenol, obtaining the appropriate acetate in each case. The proposed mechanism for the reactions of phosphines with *(6)* is seen as insertion of the phosphorus nucleophile into the peroxide bond via a slow step leading to the pentacovalent phosphorus intermediate *(10)*. In a subsequent fast step the unstable intermediate *(10)* opens up to produce the two possible dipolar ions *(11)* and *(12)*. The ion *(11)* fragments into α-alkylstyrene *(7)* and carbon dioxide, while the dipolar ion *(12)* disproportionates into alkyl phenyl ketone *(8)* and ketene. The small amounts (8%) of *(9)* is presumably formed by internal nucleophilic displacement of phosphine oxide or phosphate from either dipolar ion. Attempts to trap the phosphorane *(10)* failed.

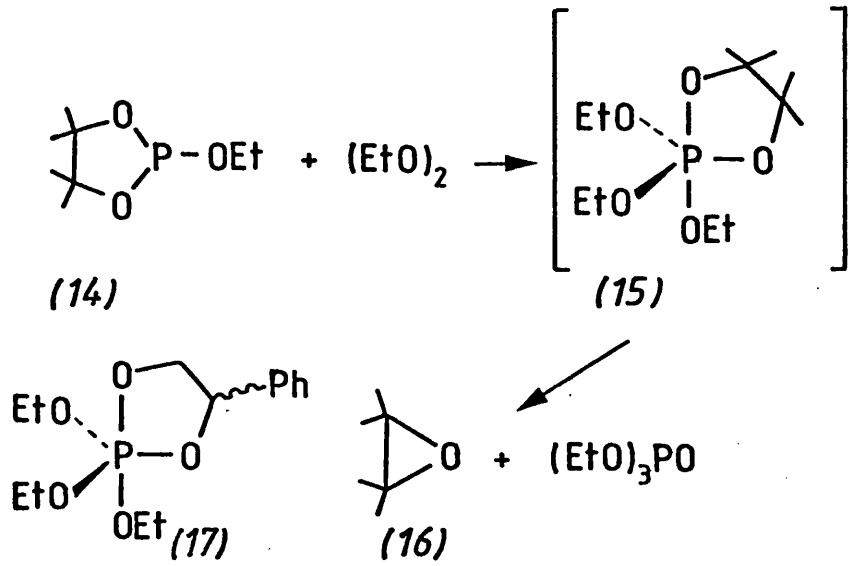
The above mechanism is supported by the work of Carles and Fliszar [5] who attempted to show the position of the attack of triphenylphosphine on an ozonide ring by the use of ^{18}O labelled ozonides *(13)*, the isotopic oxygen being situated exclusively in the ether position. They showed that in no case was the triphenylphosphine oxide labelled, thus indicating that the attack of triphenylphosphine took place very selectively on the peroxidic oxygens of these ozonides.



(13)

Furthermore in the case of unsymmetrical ozonides there is preferential loss of the more positive and the less sterically hindered peroxide oxygen.

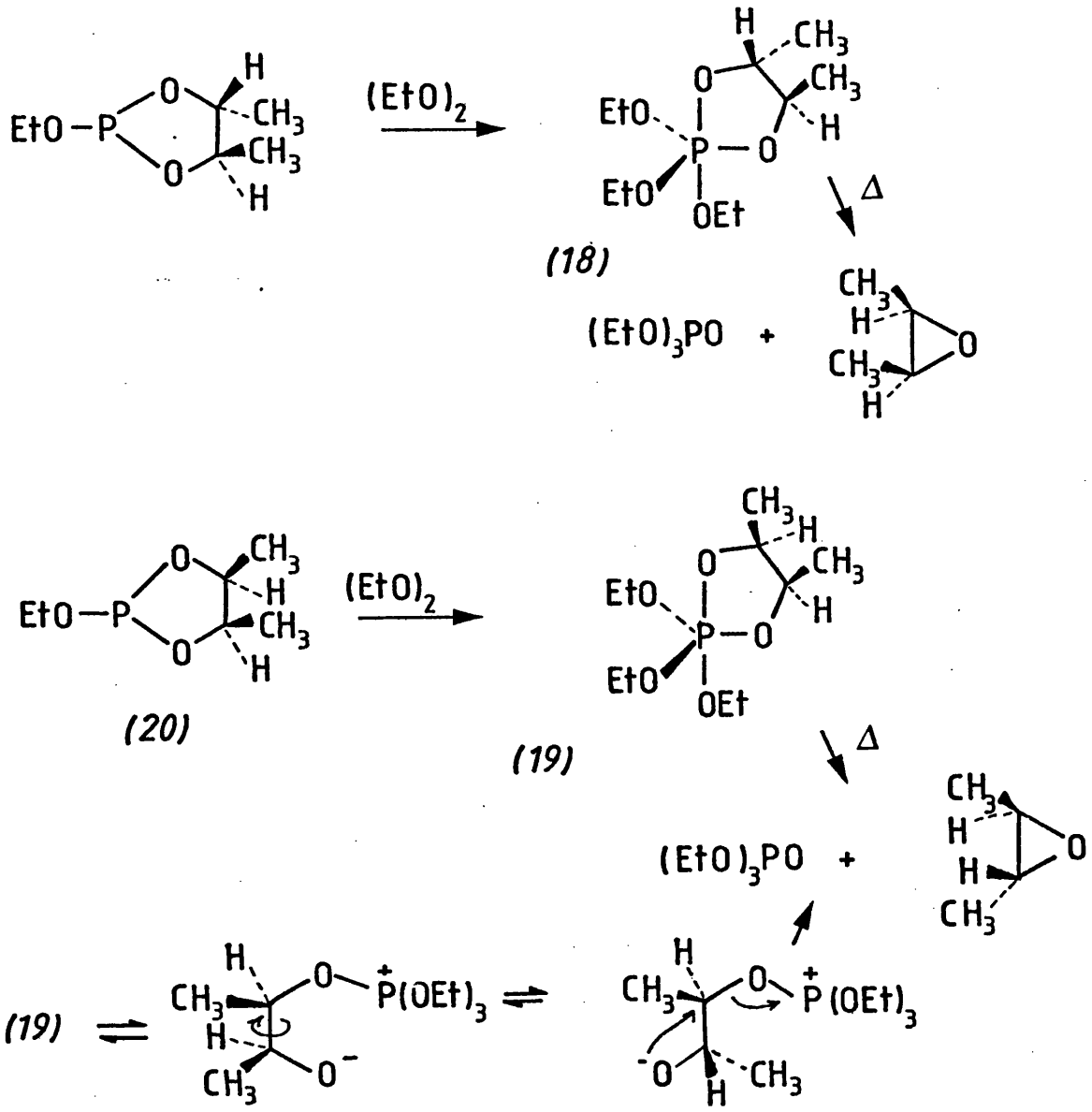
1,3,2-Dioxaphospholans [6] react with peroxide in similar reactions to those mentioned above. 1-Ethoxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan *(14)* reacts with diethyl peroxide to yield an intermediate phosphorane *(15)* which decomposes at room temperature, to give tetramethylethylene oxide *(16)* and triethyl phosphate.



The phosphorane *(17)* on the other hand was stable at room temperature but decomposed on pyrolysis at 120°C for seventeen hours with the formation of styrene oxide and triethyl phosphate.

Formation of the epoxide *(16)* was shown to be stereospecific as evinced by the decomposition of the phosphoranes *(18)* and *(19)*. These were prepared from a mixture of d,l-phosphite (88%) and meso-phosphite which gave 85% cis-but-2-ene oxide and 15% trans-but-2-ene oxide. The stereochemistries of the decomposition of *(18)* and *(19)* suggested a mechanism in which a ring P-O bond is cleaved, followed by a rotation about the C-C bond and displacement of triethyl phosphate (Scheme 2).

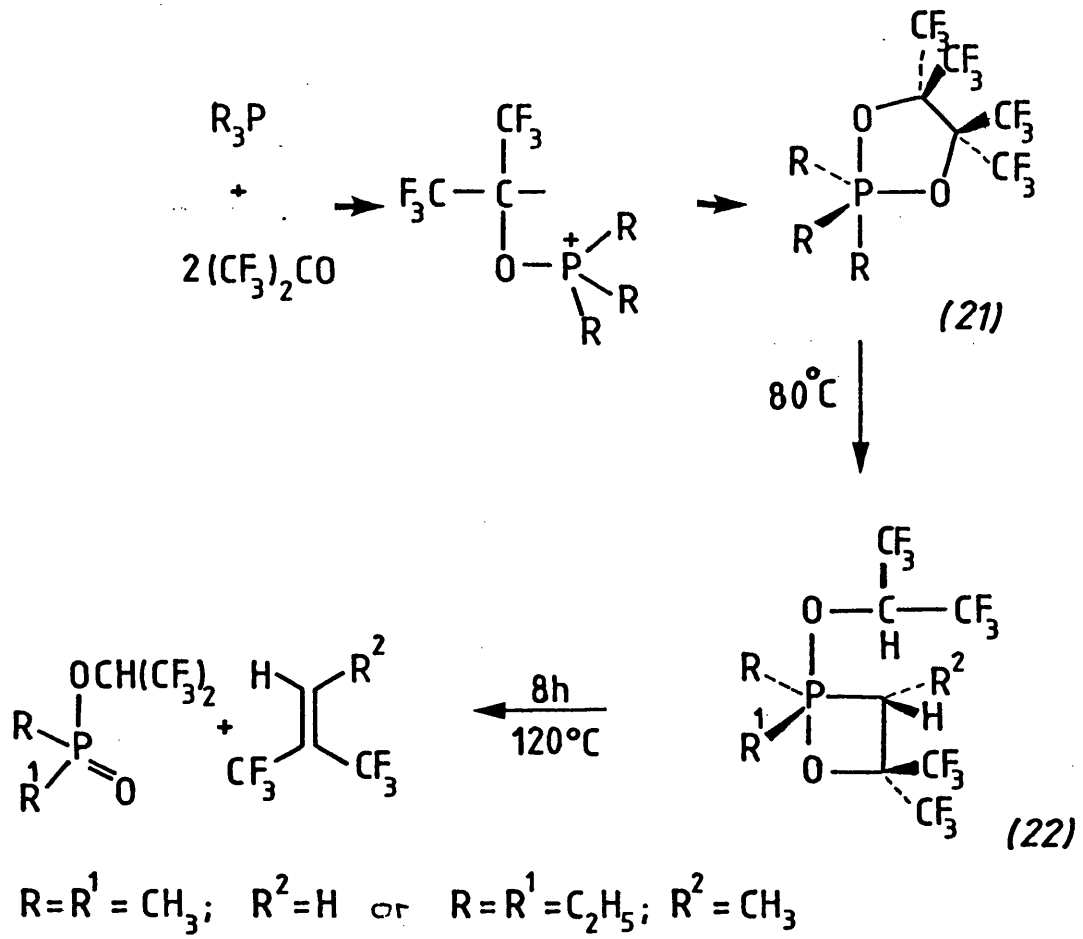
These fragmentation reactions are not the only way in which monocyclic 1,3,2-dioxaphospholans can decompose. Ramirez et al. [7] have shown that trivalent phosphorus compounds react with two moles of hexafluoroacetone to produce 1,3,2-dioxaphospholans *(21)*. These phosphor-



SCHEME 2

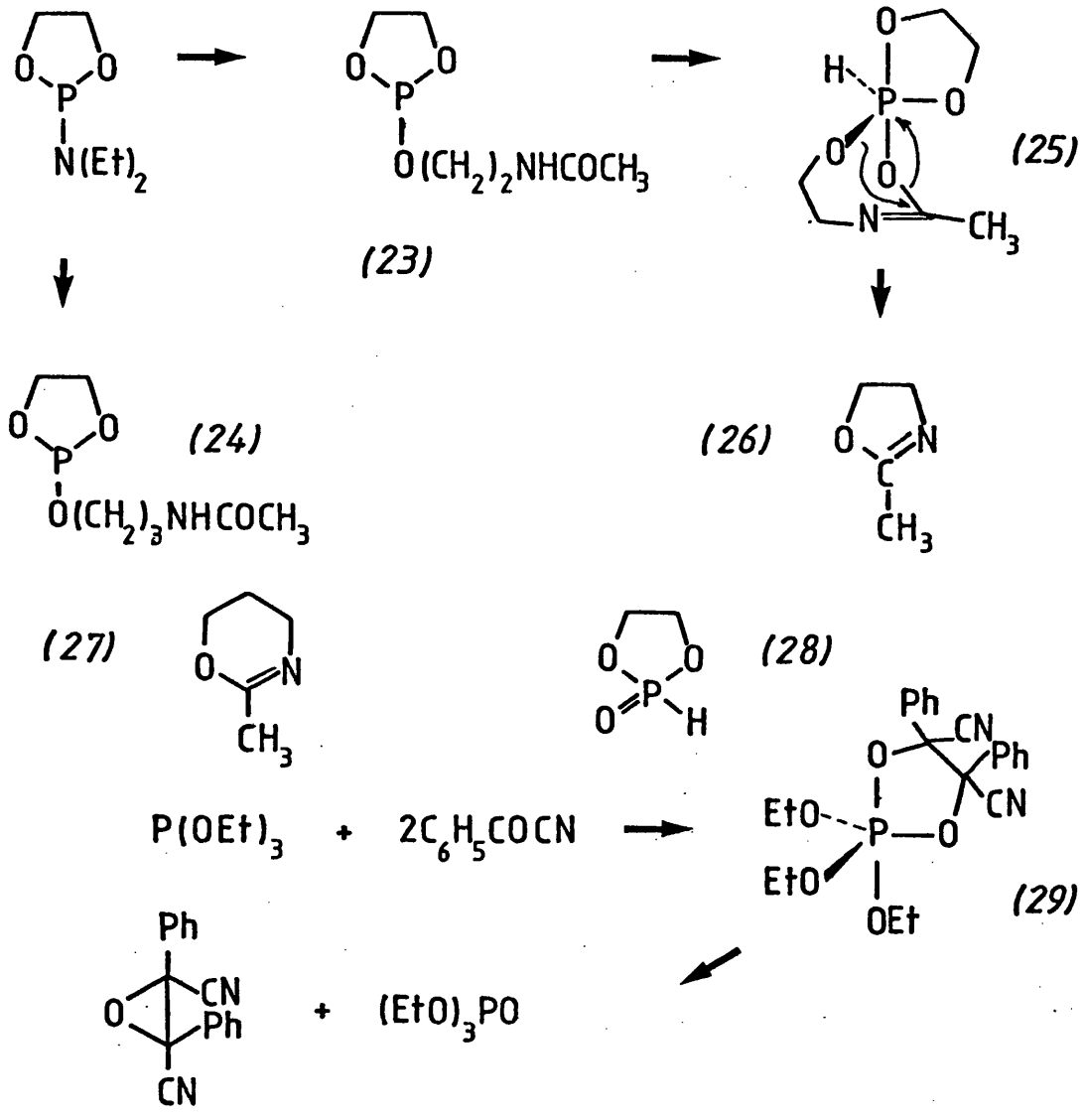
anes were thermally stable at room temperature but on heating at 80°C they decomposed to form 1,2-oxaphosphetans *(22)*. Upon further heating, 120°C for eight hours, the oxaphosphetans themselves fragmented to give ethylenes and phosphinite esters. It was suggested that the mechanism for this breakdown closely resembles that of the Wittig olefin synthesis.

Details of the thermolysis of a P(III) dioxaphospholan have appeared in which the proposed intermediate was a phosphorane [8]. 2-Diethylamino-1,3,2-dioxaphospholan reacted with N-2-hydroxyethylacetamide and

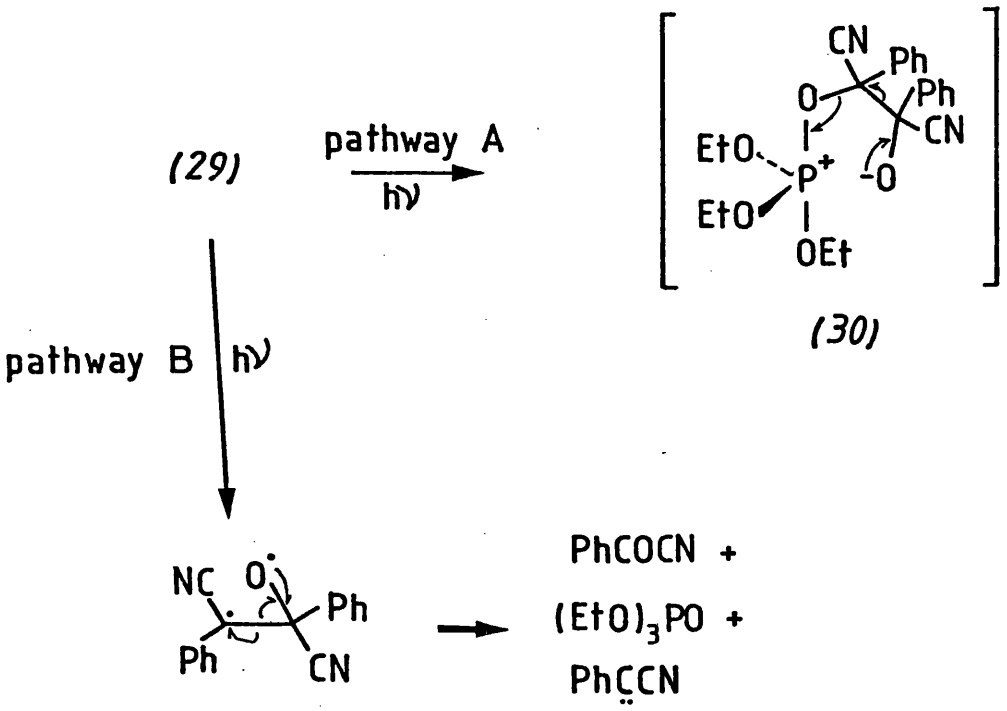


N-3-hydroxypropylacetamide to give the dioxaphospholanes *(23)* and *(24)* respectively. When *(23)* is heated at 140°-145°C in a vacuum, a volatile product is obtained in 55% yield. It was proposed that *(23)* had undergone a thermal breakdown via the phosphorane *(25)* and that the product is 4,5-dihydro-2-methyloxazole *(26)*. The dioxaphospholan *(24)* forms 5,6-dihydro-methyl-4H-1,3-oxazine *(27)* [8] via a similar mechanism, and in both cases the other product formed was shown to be polymeric 1,3,2-dioxaphospholan-2-oxide *(28)*.

The thermolysis of the 1,3,2-dioxaphosph(V)olan *(29)* has been shown [9] to give trans-2,3-dicyano-2,3-diphenyloxiran and triethyl phosphate. Irradiation with u.v. light of *(29)* in alkene solvents led to the


N(Et)2
O(CH2)2NHCOCH3
(23)
(25)
(24)
O(CH2)3NHCOCH3
(26)
(27)
(28)
P(OEt)3 + 2C6H5COCN
(EtO)3PO

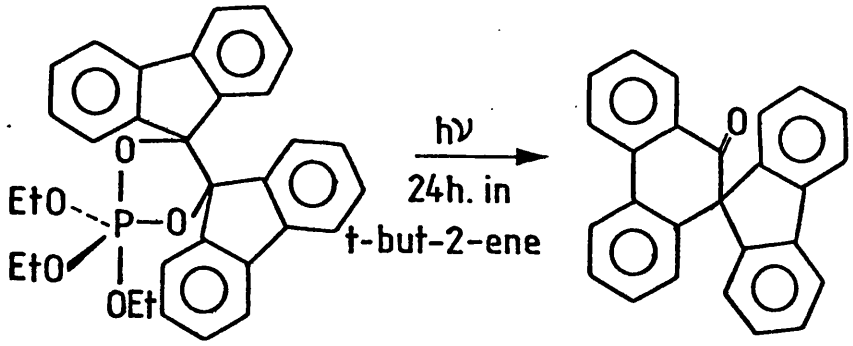
formation of cyclopropanes in comparable yields to those obtained when the oxirans themselves were photolysed. In both cases phenylcyano-carbene had been trapped. It was shown that the oxirans themselves are not the intermediates in the photolysis of *(29)* and that the reaction must proceed via one of the pathways shown in Scheme 3, route A being a heterolytic bond cleavage, via compound *(30)*, and route B a homolytic bond cleavage, of the P-O bond of *(29)*.



SCHEME 3

Petrellis also reported the photolysis of the dioxaphospholan *(31)* which gave the interesting spiro-ketone *(32)* as the major product. It is noted that this ketone was also the major product obtained in the thermolysis of *(31)* [10].

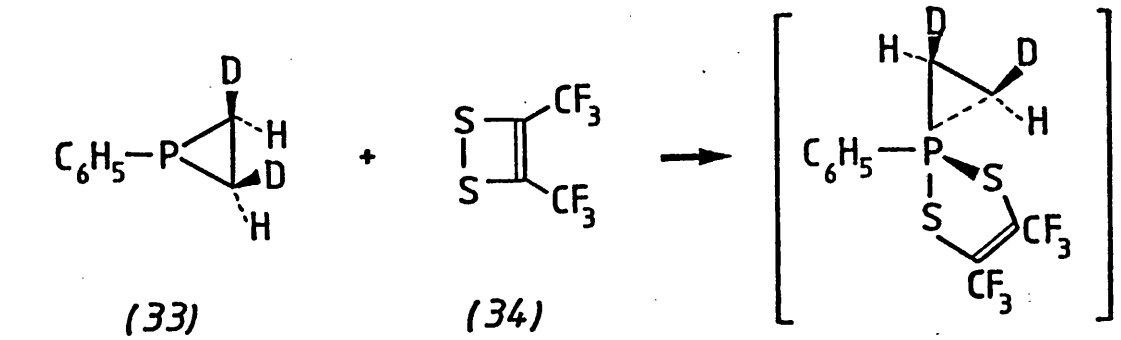
The reaction of dithieten with trisubstituted phosphorus compounds can yield phosphoranes with two sulphur atoms bonded to phosphorus. The phosphoranes show the same order of stability as has been reported for oxyphosphoranes, that is four- and five-membered ring-containing materials are usually more stable and the greater the number of electronegative groups bonded to phosphorus, the greater the stability.



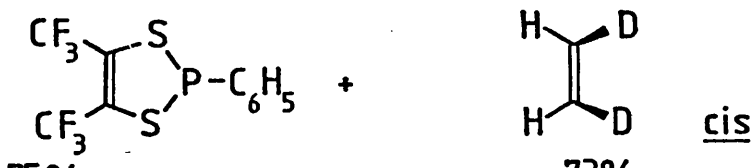
(31) *(32)*

In a qualitative way it appears that sulphur containing phosphoranes are less stable than the oxyphosphoranes [11].

When phenylphosphiran *(33)* is allowed to react with the dithieten *(34)* at -78°C in methylene chloride the products isolated are the phosphine *(35)* and cis-1,2-dideuteroethylene [12].



(33) *(34)* *(36)*

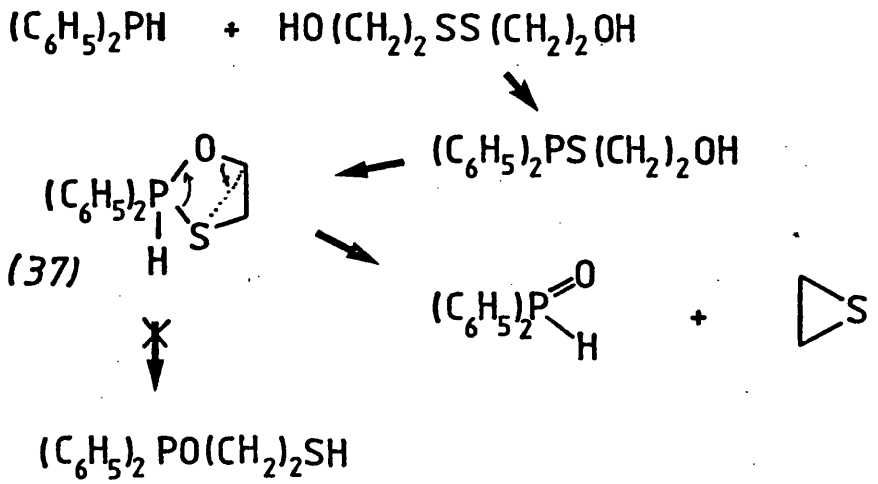


75% *(35)* 73% cis

The reaction proceeded via the phosphorane *(36)* which could decompose in one of two ways; (i) a concerted elimination reaction or (ii) a two-step process, homolytic or heterolytic cleavage followed by elimination in which the second step is faster than rotation about the C-C bond.

The reaction is so fast at -78°C that the P-C bond energy would have to be small to account for the rate of the reaction. As there seems to be no reason why the bond energy should be so low in *(36)*, a concerted process more readily accounts for the rapidity of the reaction.

A similar reaction to that of compounds *(23)* and *(24)* was proposed for the reaction of diphenylphosphine and 2-hydroxyethyl disulphide. The intermediate was assumed to be the 1,3,2-oxathiophospholan *(37)*, which it was felt rearranged by a synchronous intramolecular rearrangement. The 'driving force' of which was the formation of the phosphoryl bond and the favourable attack of the initial mercaptide ion, at the saturated carbon atom.

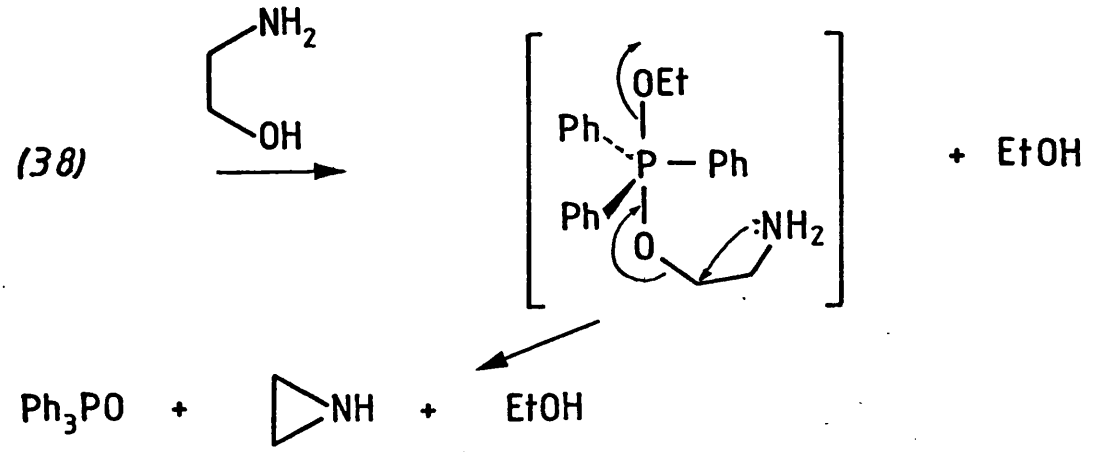


A novel route in the preparation of heterocycles has been described by Denney et al. [13,43], in which the appropriate compound is cyclised using triphenyldiethoxyphosphorane *(38)* or pentaethoxyphosphorane *(39)*.

A summary of the results is given in Table I.

$(C_6H_5)_3P(OEt)_2$ (38) $P(OEt)_5$ (39)

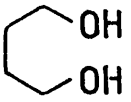
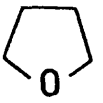
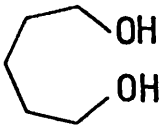
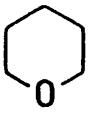
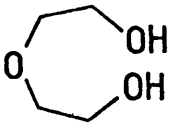
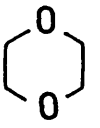
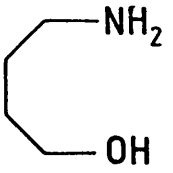
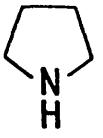
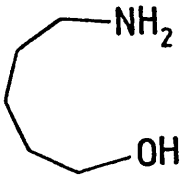
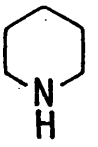
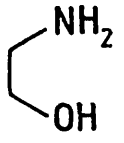
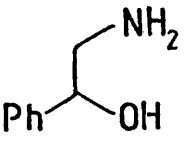
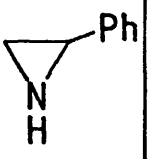
The phosphoranes react with the difunctional molecules by an initial exchange of the hydroxy group followed by a displacement reaction which yields the heterocycle, the phosphine oxide, and two moles of ethanol. It was stated that the advantages gained by the use of these reagents are that, no blocking groups are required, the reactions were carried out under mild conditions and neither acids nor bases are used as catalysts nor are they generated during these cyclisations. It could be added that the reactions proceed, in most cases, in high yields.



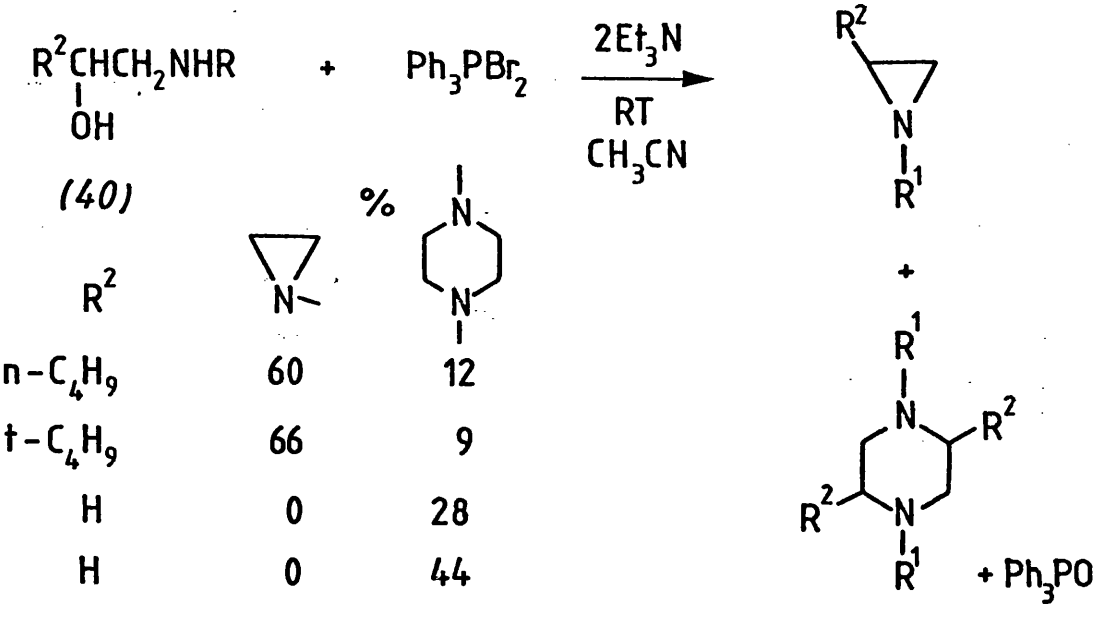
Similar cyclisation reactions have been reported by Japanese workers [14], 2-aminoalcohols *(40)* being converted into aziridines and piperazines using dibromotriphenylphosphorane. They found that for 2-substituted 2-aminoalcohols, aziridines were the major products, piperazines being the minor products. Attempted preparations of 1-

TABLE I

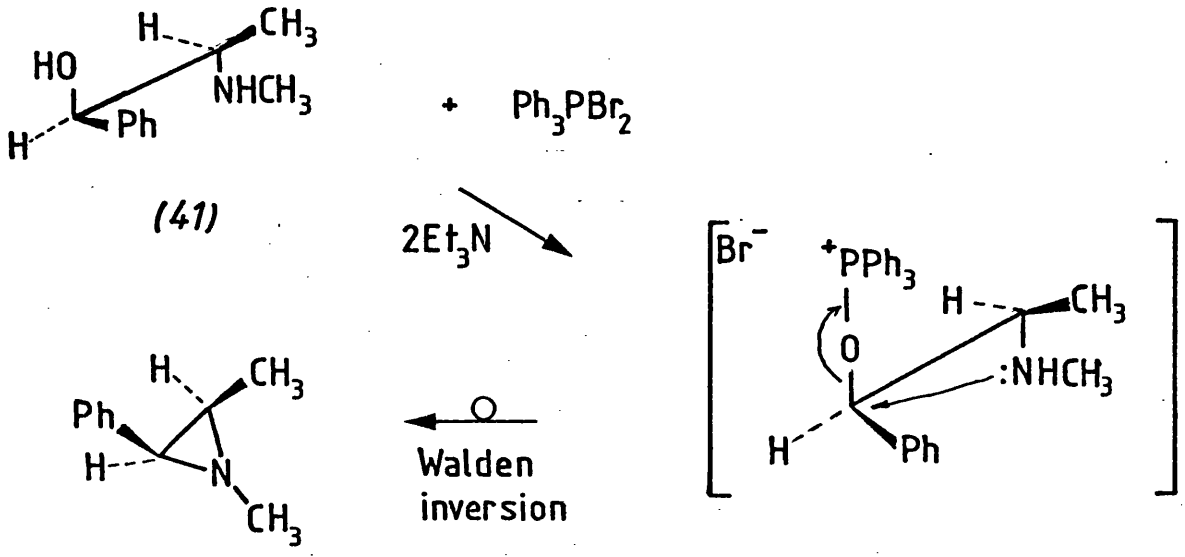
SOME SYNTHETIC APPLICATIONS OF DIETHOXYPHOSPHORANES

Phosphorane	Diol	Heterocyclic Product	Yield
(39)			87%
(39)			26%
(38)			90%
(38)			78%
(38)			85%
(38)			70%
(38)			91%

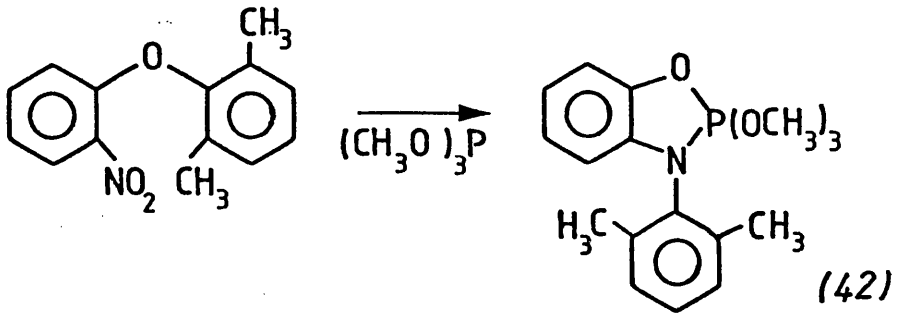
monosubstituted aziridines using similar conditions lead only to piperazines.



D (+)-threoephedrine *(41)* when reacted with dibromotriphenylphosphorane and two moles of triethylamine gave L (-)cis-1,2-dimethyl-3-phenylaziridine in 74% yield. The reaction proceeds by an inversion of configuration in the ring-closure step. This tends to rule out a phosphorane intermediate unless the reaction proceeds via a phosphorane decomposing into a betaine which rotates about the C-C bond and eliminates triphenylphosphine oxide.

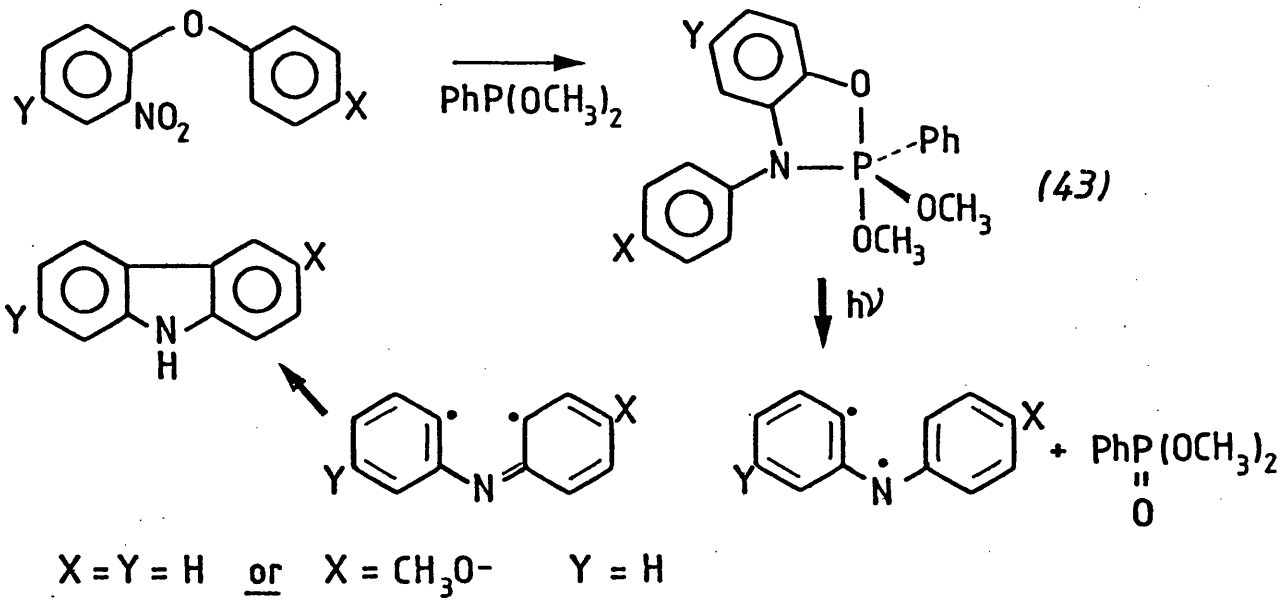


Cadogan [15] has reported the preparation of a number of phosphoranes from the reaction of P(III) compounds with aromatic nitro (and nitroso-) species. In some cases stable phosphoranes e.g. *(42)* are obtained.



(42)

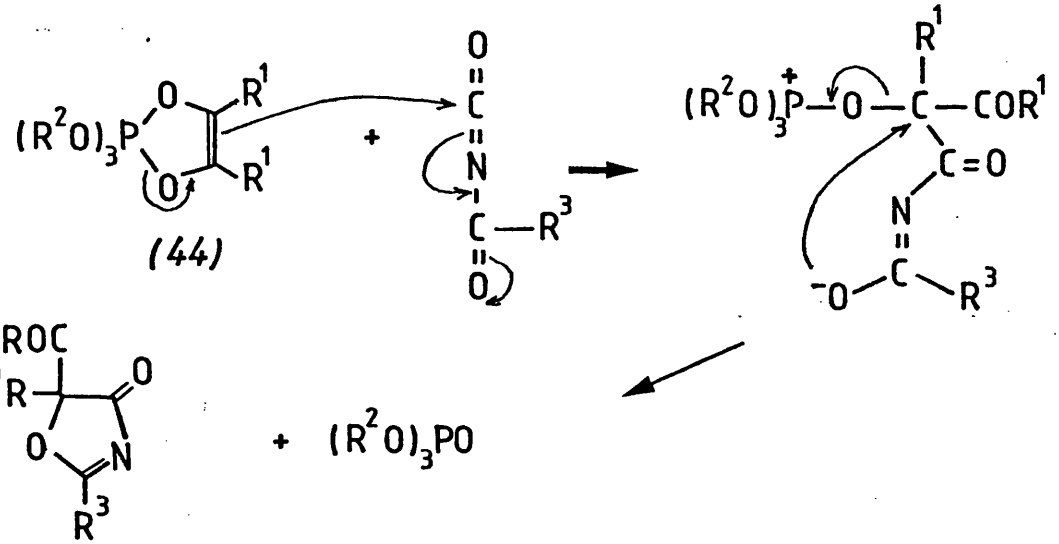
It was found that the phosphoranes *(43)* would decompose, when irradiated in benzene with a medium pressure mercury lamp (pyrex filter) [16], to give moderate yields of carbazoles and dimethyl phenylphosphonate as shown in Scheme 4. This constitutes a simple two-step deoxygenation reaction from the readily available ethers.



SCHEME 4

The dioxaphospholene *(44)* ($R^1 = CH_3$, $R^2 = CH_3$) reacts with benzoyl isocyanate [17] (R^3 = Ph) at 30°C to give 2-phenyl-5-acetyl-5-methyl-2-oxazolin-4-one *(45)* (R^3 = Ph) in good yields. No intermediate was

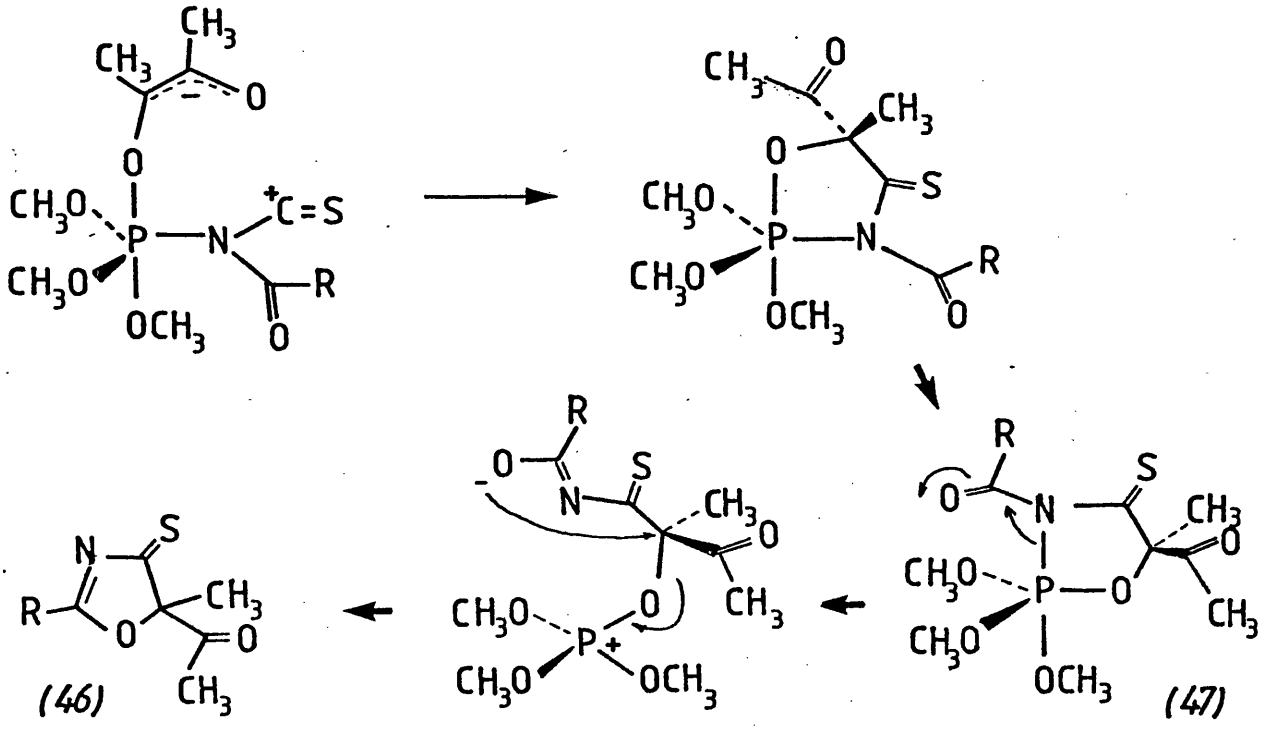
detected during the reaction but again it was assumed that the phospholene reacted via a dipolar adduct which underwent an intramolecular displacement of trimethyl phosphate to yield the products.



(44)

(45)

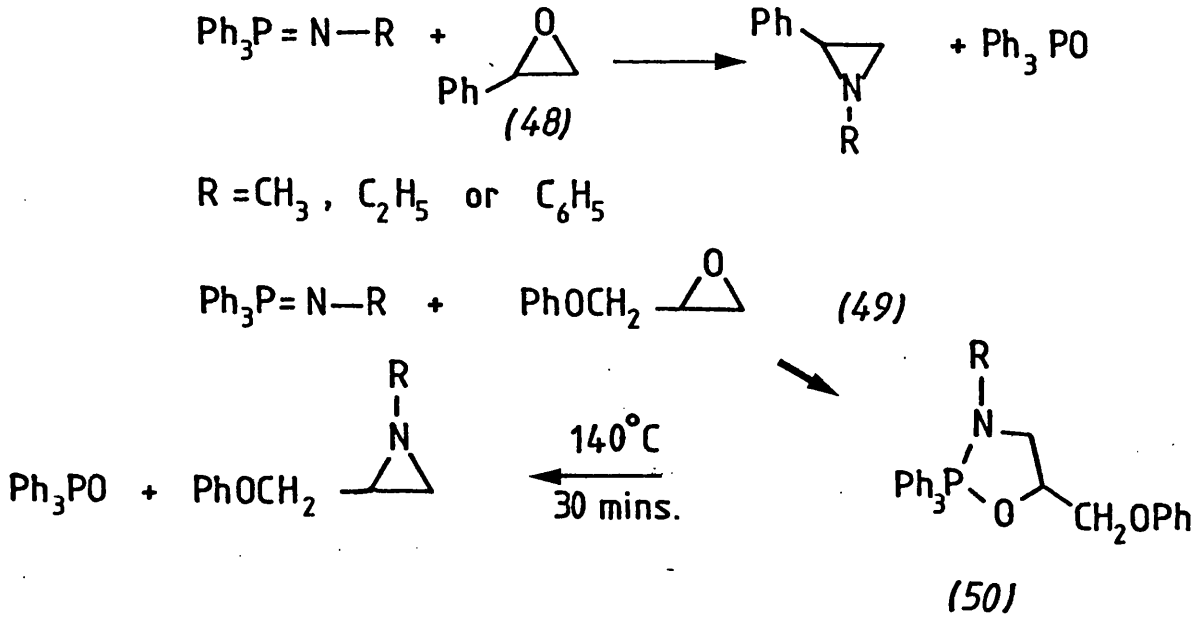
Ramirez has also shown [18] that although isothiocyanates, R-N=C=S, fail to react with dioxaphospholenes, N-acylisothiocyanates, R^3CO-N=C=S, react by an analogous reaction to that of benzoyl isocyanate to give 2-oxazolin-4-thiones *(46)*, the only difference being the initial step in which the co-ordination of the slightly more electronegative nitrogen rather than sulphur leads to the formation of a 1,3,2-oxazaphospholan *(47)* as opposed to a 1,3,2-dioxaphospholan as an intermediate. See also [19, 20 and 21].



(46)

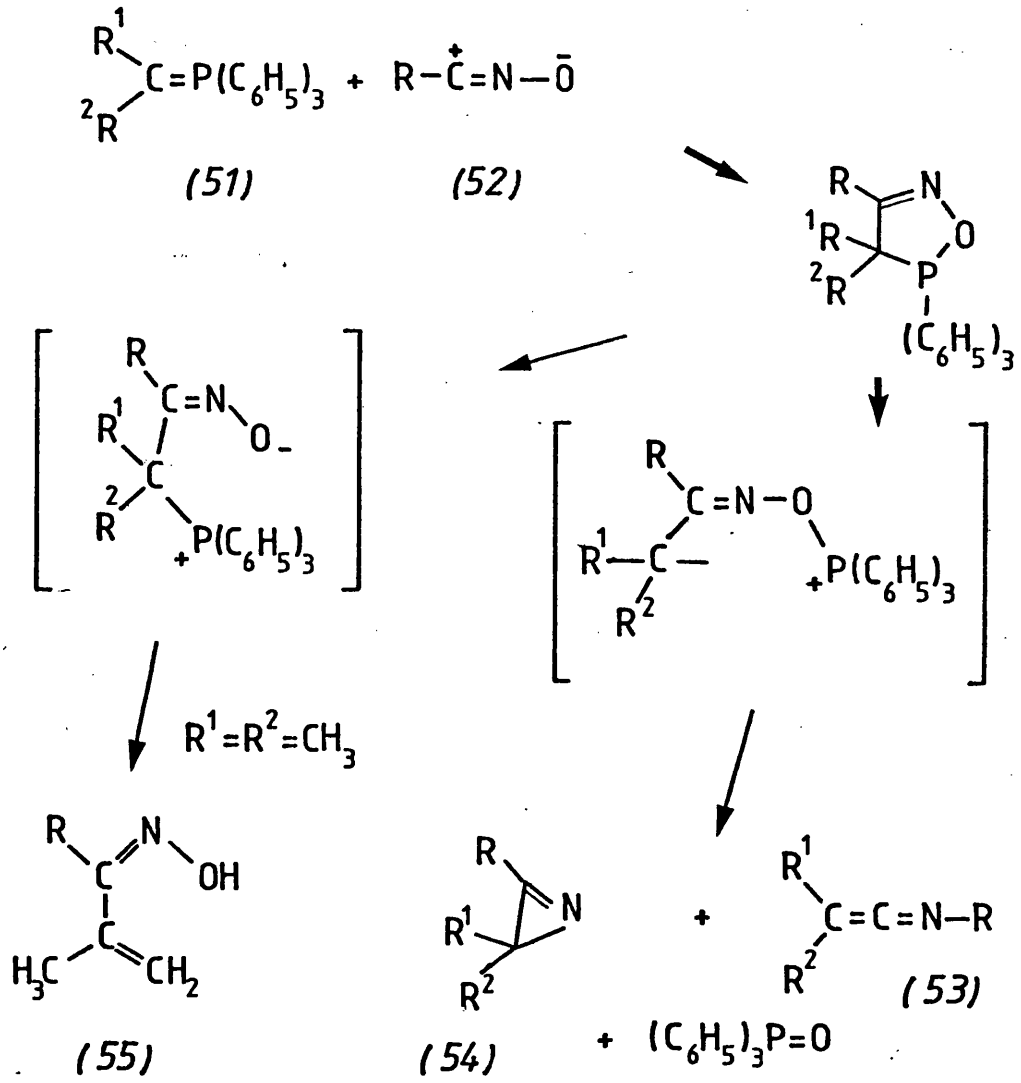
(47)

A reaction which has been shown [22] to involve the fragmentation of a phosphorane is the reaction between the oxiranes *(48)* and *(49)* with N-substituted iminophosphoranes. The reaction of *(49)* initially yields the stable 1,3,2-oxazaphospholan *(50)* which upon heating fragments to give aziridines,



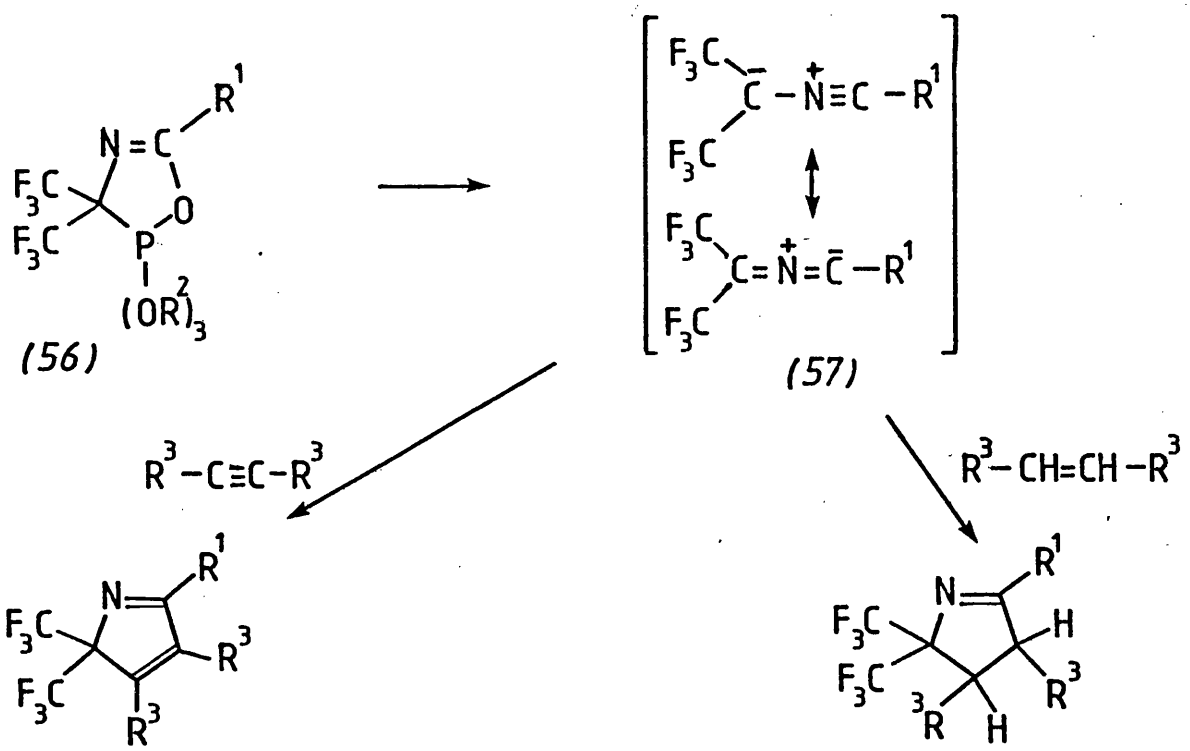
presumably *(48)* proceeds via a similar mechanism involving a thermally unstable phosphorane.

The ylides *(51)* react with nitrile oxides *(52)* to give 4,5-dihydro-1,2,5-oxazaphospholenes [22,23]. These are thermally unstable, the rate of their decomposition depending on the substituents, R, R^1 and R^2. When R^1 and R^2 have negative inductive (-I) and mesomeric (-M) effects then the ketenimines *(53)* are formed, whereas when both are electron donating, azirines *(54)* are the products, in each case triphenylphosphine oxide is the other product. When R exerts a -I effect and simultaneously R^1 and R^2 a +I effect then the phosphorane decomposes by loss of triphenylphosphine and formation of the α,β-unsaturated oxime *(55)*. The 1,3,5-oxazaphosphol-3-ene *(56)* undergoes



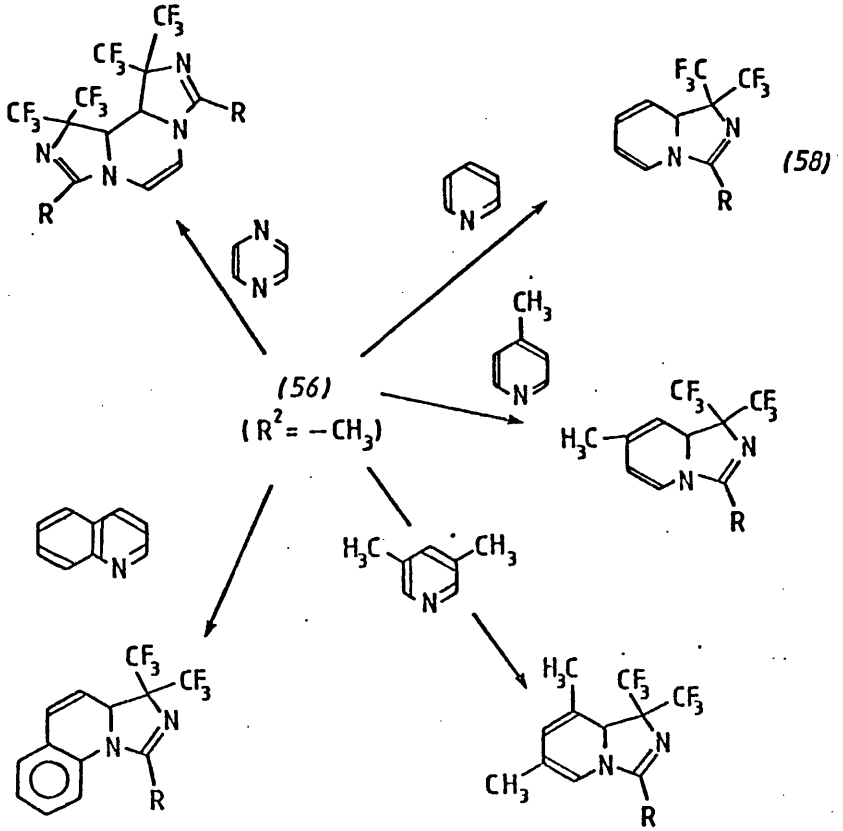
thermal and photochemical cyclo-elimination of phosphoric acid esters to yield nitrile ylides *(57)* which can be trapped by dipolarophiles. Unsymmetrically substituted alkynes and alkenes add across the 1,3-dipole in either direction giving two products in each case [24,116]. Similarly, when *(56)* is heated at 140°C for twenty-four hours in pyridine, moderate yields of *(58)* are obtained [25]. The same type of reaction is observed for a whole range of nitrogen heterocycles, presumably involving also the 1,3-dipolar species.

Hall [26] has shown that the reaction of cis, cis *(59)* and cis, trans-1,2,5-trimethylphosphol-3-ene *(60)* with diethyl peroxide in cyclopentane results in the formation of trans, trans-hexa-2,4-diene *(61)* in quantitative yield, together with diethyl methylphosphonite.



(56) (57)

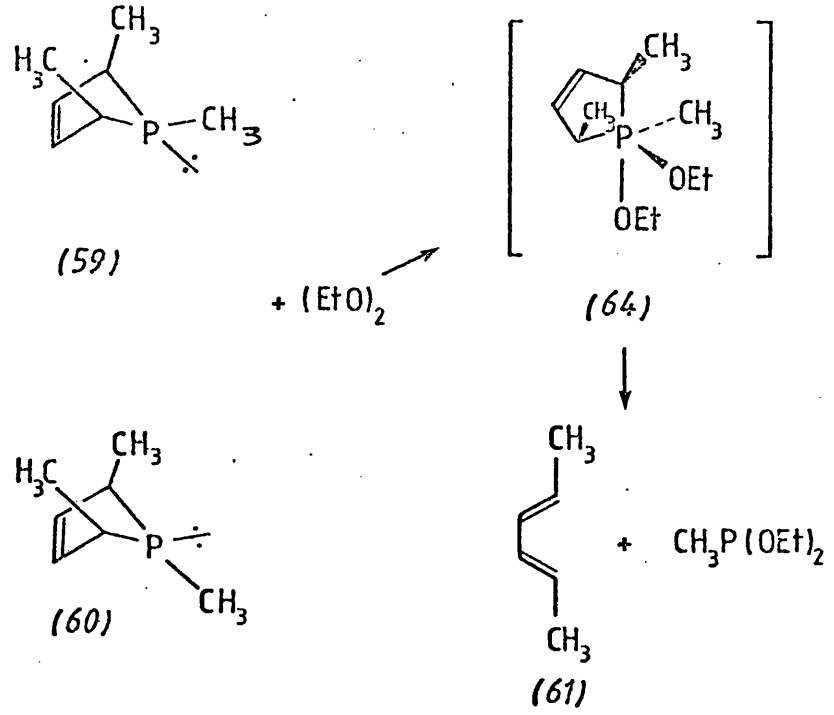
The reaction being 99% stereospecific, it may proceed via a concerted disrotatory, $4\pi + 2\pi$ electron fragmentation reaction.

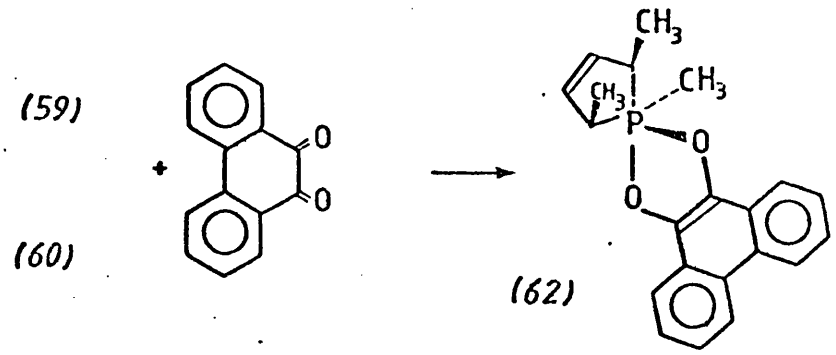


(58)

Hall also shows that the reaction of phenanthraquinone with the 1,2,5-trimethylphosphol-3-enes *(59)* and *(60)* in deuterochloroform at 25°C,

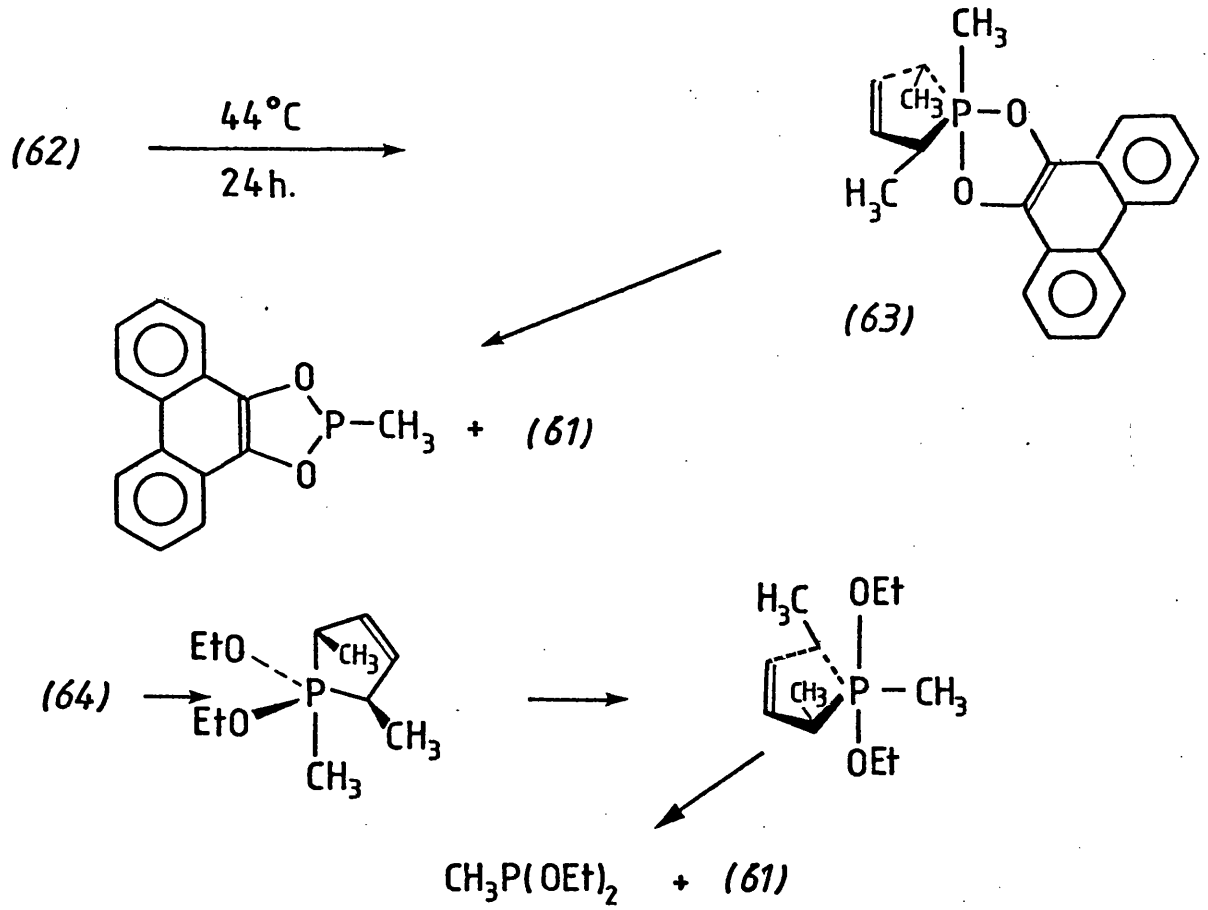
gave stable phosphoranes *(62)*. Considering the normal strain and polarity rules it seems reasonable that *(62)* prefers the conformation shown.





+ diastereoisomer

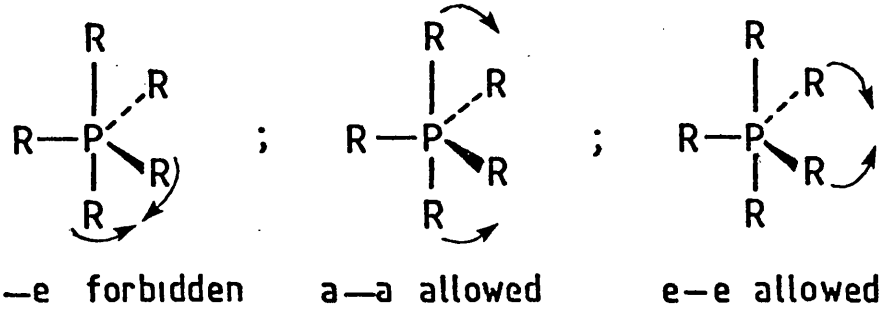
As the free energy of activation for the fragmentation of *(62)* is much larger than that for *(64)*, more than that expected going from mono- to bicyclic phosphoranes, it was concluded that the former must undergo a pseudorotation first to *(63)* which facilitates an e,e loss. With *(64)* the energy lost in placing the ring e,e is compensated for by having the two ethoxy groups apical. Hence the difference in free energy probably arises from this energetically unfavourable pseudo-rotation.



Hoffmann [27] has considered the theoretical fragmentation of PR_5 from the standpoint of orbital symmetry calculations.

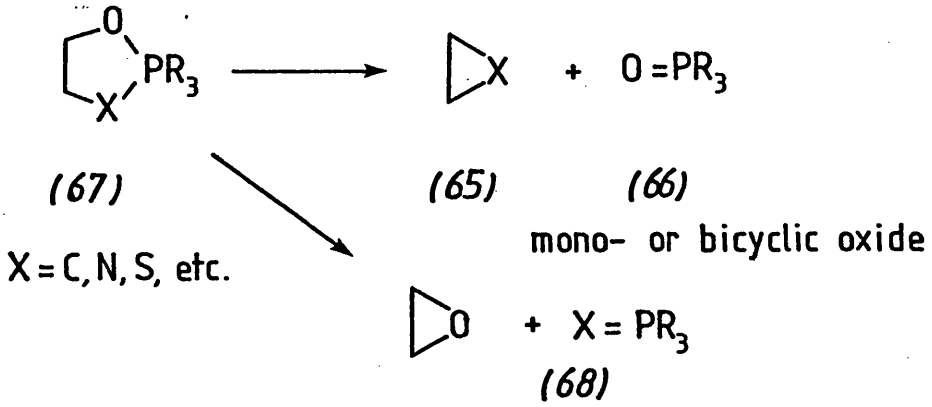
$$PR_5 \longrightarrow PR_3 + R_2$$

He concluded that from a trigonal bipyramidal structure (D_{3h}) the allowed processes were e-e or a-a departure of R_2. Whereas the least motion pathway, e-a, was symmetry forbidden.



In general, systems such as *(67)* will fragment to *(65)* and *(66)*, the 'driving force' being the formation of the strong P=O bond. The alter-

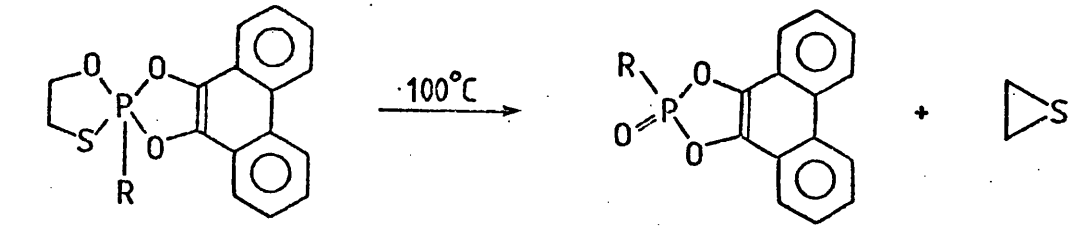
native route would give the less stable P=X bond in *(68)* which has not enough energy of formation to compensate for the 3-membered oxiran ring.



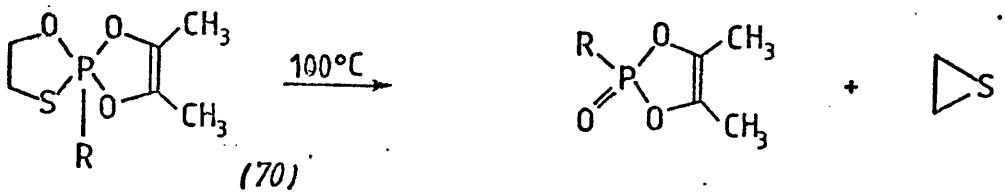
Similarly in the bicyclic systems *(69)* and *(70)* ethylene sulphide and not oxiran is the product in each case [28].

The preference for P=O bond formation can be of great synthetic use because it acts as a 'driving force' for many reactions providing energy to compensate for otherwise unfavourable fragmentations.

Carbethoxymethylenetriphenylphosphorane *(71)* reacts with styrene oxide to form the 1-carbethoxy-2-phenylcyclopropane <u>via</u> the intermediates *(72)* and *(73)* [29].

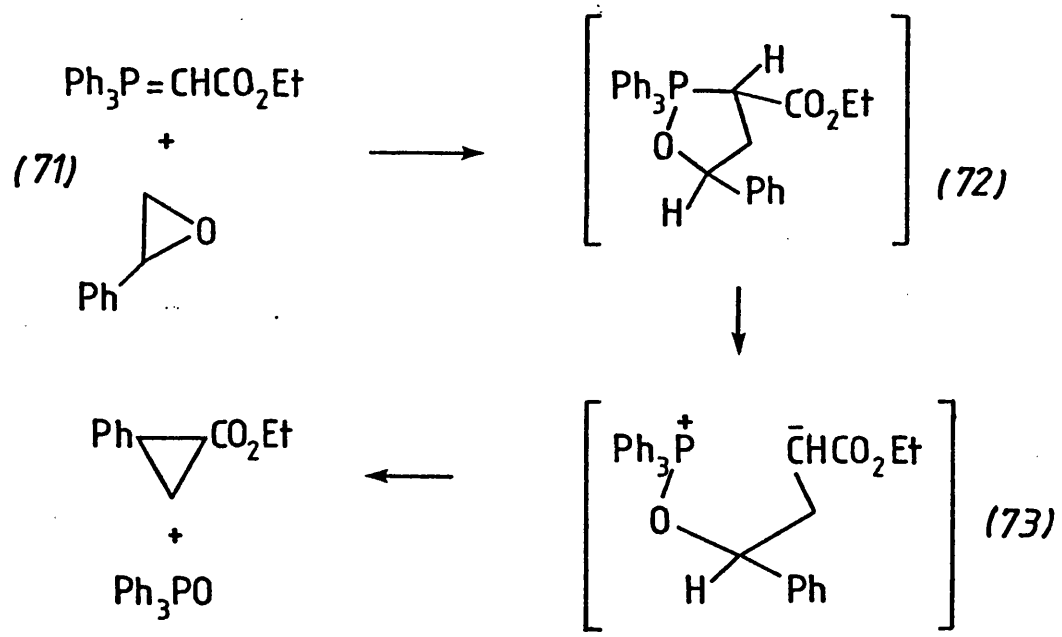


R=Ph or t-Bu *(69)*



(70)

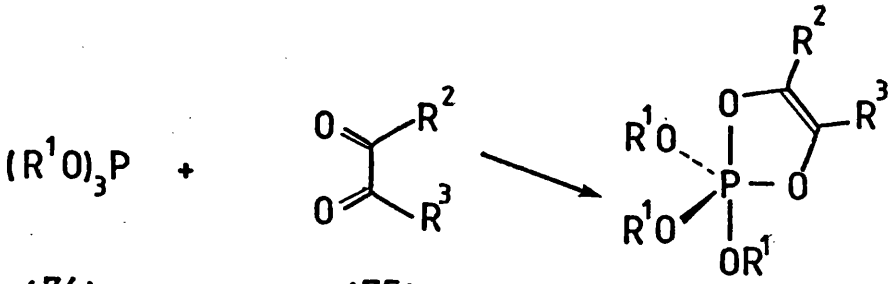
It must also be said that an alternative route for C-P-C-containing rings is the loss of a P(III) moiety and hydrocarbon by a retro-Diels-Alder $2\pi + 4\pi$ reaction [12].



THE PREPARATION OF PHOSPHORANES

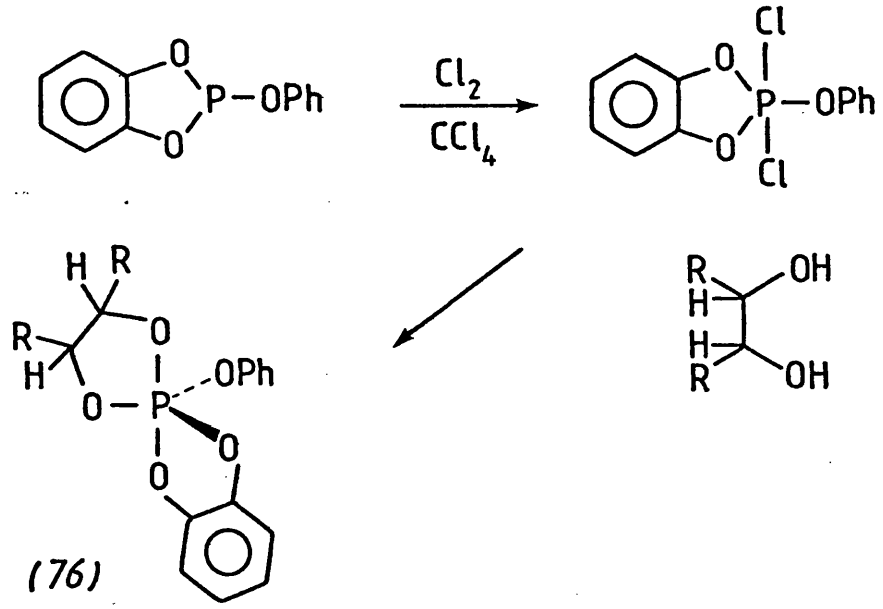
A great deal of work has gone into finding ways to prepare phosphoranes [34], some of the more general routes are mentioned below.

Phosphoranes can be prepared from trivalent compounds *(74)* by addition of two ligands, for example, adducts with 1,3-unsaturated compounds [30,31] such as α-diketones *(75)*, dienes and α,β-unsaturated carbonyl compounds. The ligands can be halogens, which in turn can be used to prepare *(76)* [32,33], peroxides (to prepare *(2)*) and similar species such as *(34)*.



(74) *(75)*

Reactive carbonyl compounds such as hexafluoroacetone also give phosphoranes such as *(21)*. Halo- and amino-phosphines react with diols or related compounds *(77)* as shown by Burgada [35,36], Wolf [142] and others [14]. One of the most useful reactions in this field is the addition of α,ω diols to trivalent phosphorus compounds using N-chloro-diisopropylamine [34,37] *(78)*.



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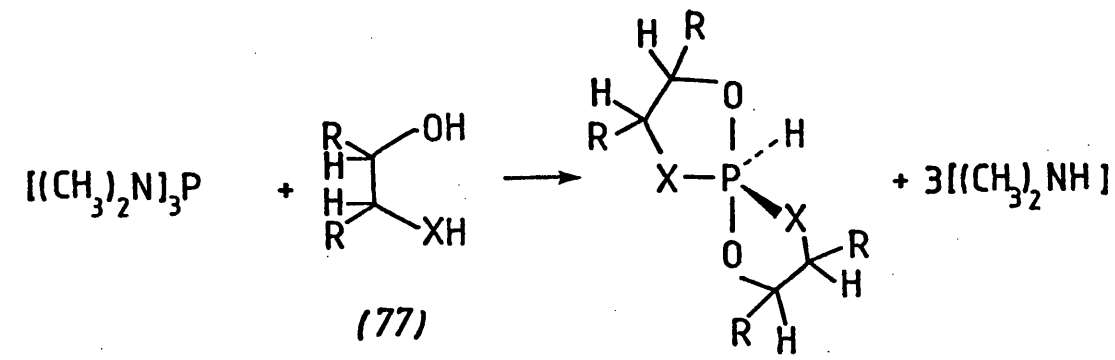

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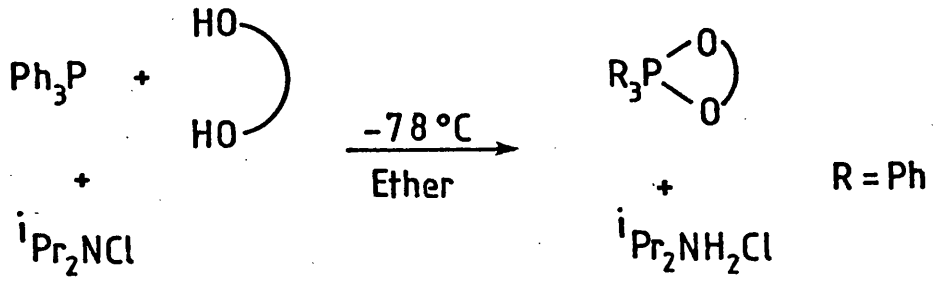
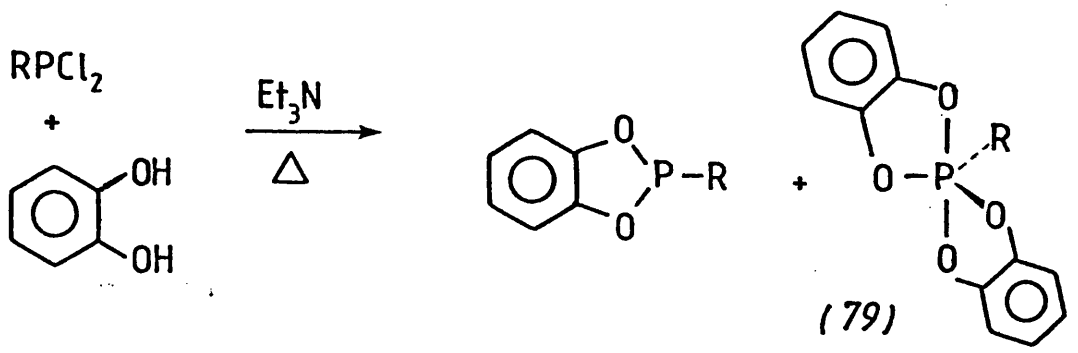


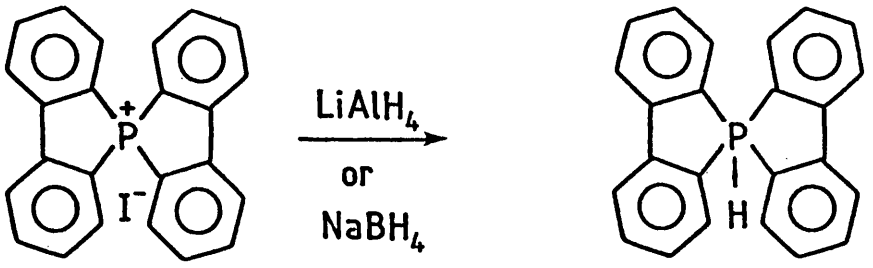
(78)

Finally a miscellaneous reaction which should be included in this section is the reaction used to form *(79)* [38], between catechol and dichlorophenylphosphine in the presence of triethylamine.

Another group of reactions using tetraco-ordinate phosphorus compounds *(80)* have been described in this case, by reduction of phosphonium salts [39,143]. Adducts can also be obtained from phos-



phine oxides *(81)*, using trifluoromethanesulphonic anhydride and diisopropylamine [34] or by halogenation of the oxide *(82)* with phosphorus pentachloride.



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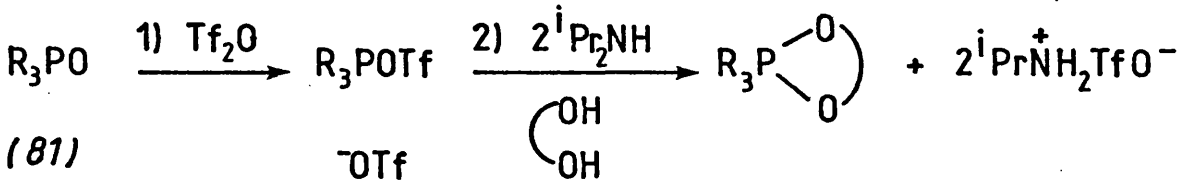
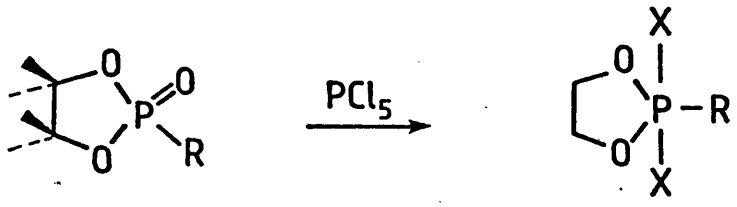
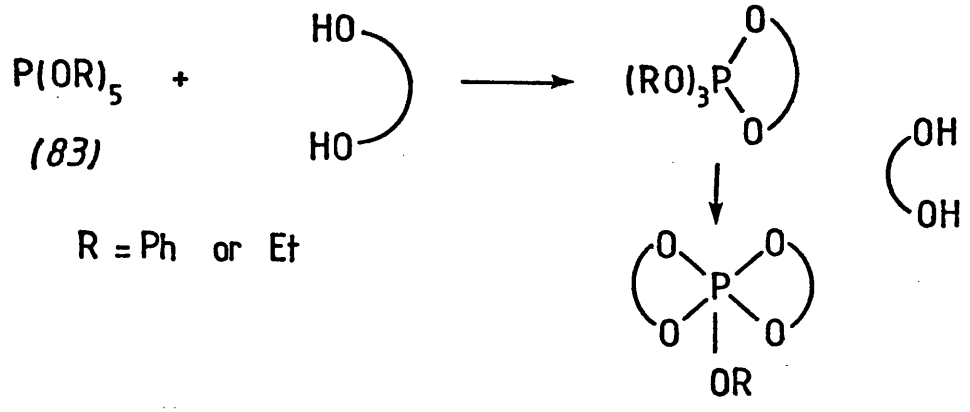


(81)



(82) X = Cl or F

The last major preparative route is that using exchange reactions [41,42,43] such as that between *(83)* and diols.

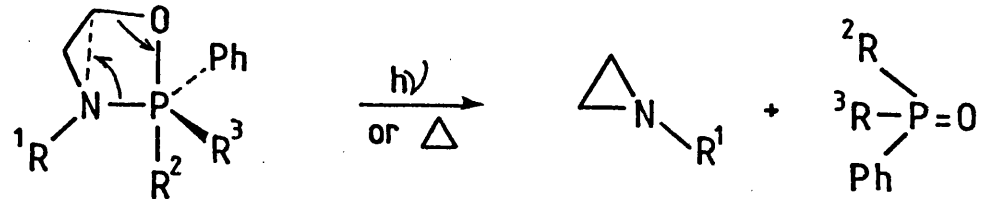


(83)

R = Ph or Et

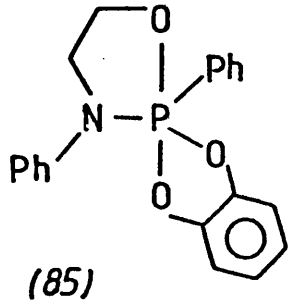
SOME REACTIONS OF OXAZAPHOSPHORANES

Oxazaphosphoranes *(43)* have been used in the synthesis of carbazoles by Cadogan [16]. It was felt that these compounds might also be used to prepare aziridines, the driving force for the reaction being the formation of a phosphoryl bond.

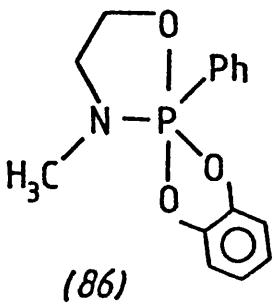


In order to further facilitate aziridine formation a mono-cyclic phosphorane would be preferred as this eliminates the possibility of competitive ring-cleavage which would give quite different products. The required phosphoranes need also to incorporate not only the nitrogen atom for the aziridine but also the oxygen atom to form the phosphine oxide.

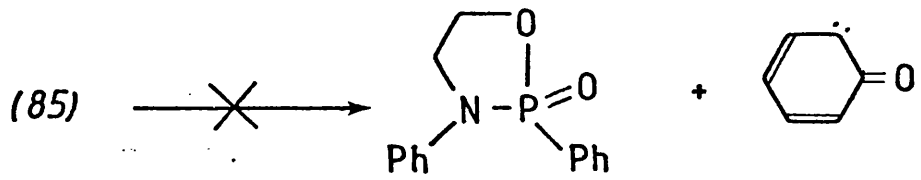
Another factor is the ease of formation of the phosphorane, if too difficult to prepare then it would be of little use to form aziridines. The phosphoranes chosen which meet two of the three criteria were the phosphoranes *(85)* and *(86)*. Although these molecules incorporate catechol rings as well as oxazaphospholans rings, the former were expected to be less likely to cleave as the products resulting from such a fragmentation would be *(87)* and *(88)*.



(85)



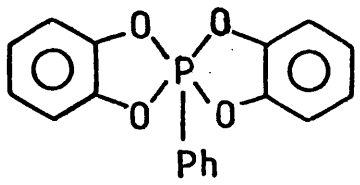
(86)



(85) (87) (88)

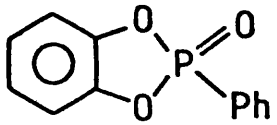
The two oxazaphosphorans prepared in moderate yields from the readily available corresponding 2-phenyl-oxazaphospholans were 5,9-diphenyl-2,3-benzo-9-aza-1,4,6-trioxa-5-phosphaspiro-[4,4]-nonane *(85)* and 9-methyl-5-phenyl-2,3-benzo-9-aza-1,4,6-trioxa-5-phosphaspiro-[4,4]-nonane *(86)* using the N-chlorodiisopropylamine method.

Attempts to distil the phosphorane *(85)* led to its decomposition. The ^{1}H n.m.r. spectrum of the reaction mixture showed a singlet at 3.45δ and the ^{31}P n.m.r. showed that as well as the phosphorane (+33 p.p.m. measured from phosphoric acid, 3% of the phosphorus containing material), six other products were present; these included 2,3-diphenyl-1,3,2-oxazaphospholan 1-oxide (-27 p.p.m. 3%), the catechol dimer *(84)*, (+10 p.p.m. 6%), polymeric phosphorus containing material (-15.7 p.p.m. 20%) and a very small amount of the ester *(89)*, (-19 p.p.m. 2%). The peak in the ^{31}P n.m.r. spectrum at -20 p.p.m. (20%) could have been phenylphosphoric acid formed from the hydrolysis of o-hydroxyphenyl hydrogen phenylphosphonate (-36 p.p.m. 46%) although none of the products could be isolated.



$^{31}P = +10$

(84)



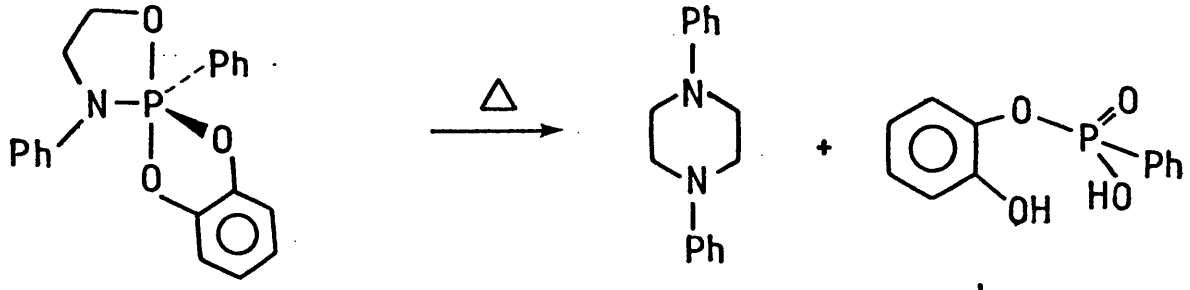
(89)

These results would be consistent with a mechanism in which the phosphorane fragmented by cleavage of the phosphorus-nitrogen bond, Cadogan suggested a radical mechanism, and initial formation of the ester *(89)*. This ester had been shown by Berlin [44] to be extremely unstable and to hydrolyse quantitatively to o-hydroxyphenyl hydrogen phenylphosphonate, although the major ^{31}P n.m.r. peak observed in the spectrum of the reaction mixture was -36 p.p.m., a value which might have been a little lower than expected for this compound. Hydrolysis of the product would have led to the formation of phenylphosphoric acid.

The polymeric product would have resulted at the same time as the dicatechol species *(84)* whereas the oxazaphosphinoline oxide would have been formed by the cleavage of catechol from the phosphorane and oxidation of the phosphine. The non-phosphorus containing product unfortunately was not N-phenylaziridine but either N,N′-diphenylpiperazine or poly-N-phenylethylenimine. To study this decomposition more fully, N-phenylaziridine was prepared in a separate experiment using a modified Gabriel synthesis. When N-phenylaziridine was heated under nitrogen at 135°C for ninety minutes no reaction occurred; after eighteen hours at 200°C 50% of the N-phenylaziridine had decomposed and formed polymer, the remaining 50% being unreacted starting material. Conversion to polymer was quantitative when a small amount of ethanol was present. These results are consistent with the findings of Heine [49]. An attempt was made to trap an intermediate in the polymerization using indene; starting material was, however, recovered unreacted.

Heine [49] has shown that N-phenylaziridine was relatively unstable and could be converted by stirring in water to poly-N-phenylethylenimine. The thermolysis of *(85)* under nitrogen showed that one of the products

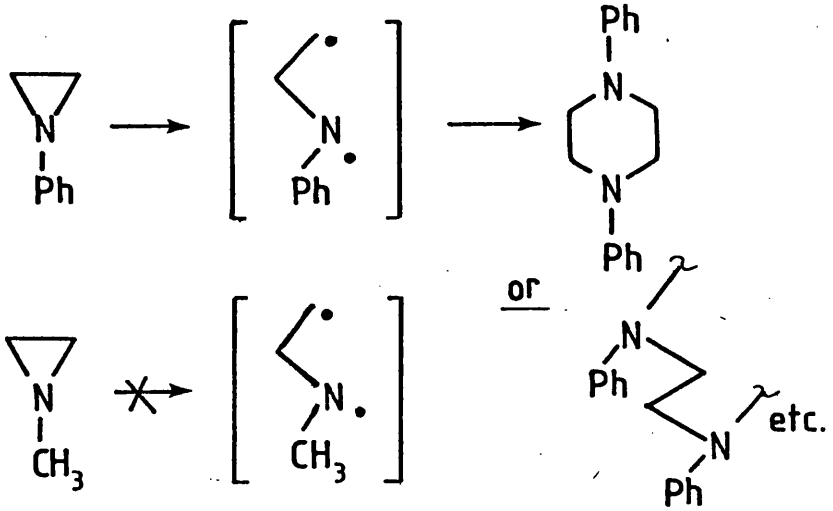
obtained was N,N′-diphenylpiperazine; this was confirmed by a mixed melting point.



(85)

The aim of using the phosphorane *(85)* as a means to the synthesis of N-phenylaziridine clearly was unsuccessful; however it seems likely that the required products may have been formed in the original reaction mixture but during the obtaining of spectral details of these products they were hydrolysed.

When *(85)* was photolysed in methanol ($\lambda = 254$ nm) the N,N′-diphenylpiperazine was also formed as shown by ^{1}H n.m.r. spectral evidence; however it could not be isolated. Also appearing in the ^{1}H proton n.m.r. spectrum was a doublet characteristic of a phosphorus-methoxide grouping, this was presumably dimethyl phenylphosphonate.



SCHEME 5

The vacuum flash thermolysis (VFT) of 9-methyl-5-phenyl-2,3-benzo-9-aza-1,4,6-trioxa-5-phosphaspiro-[4,4]-nonane *(86)* at 750°C gave four products as well as unreacted starting material (^{31}P n.m.r. + 30 p.p.m., 22%).

The products obtained were identified as o-hydroxy-phenyl-hydrogen-phenylphosphonate (-36 p.p.m., 13.5%), 3-methyl-1-phenyl-1,3,2-oxaza-phospholan 1-oxide (-33 p.p.m., 35%), phenylphosphonic acid (-18.5 p.p.m., 55%) and an unidentified, probably polymeric product (-16 p.p.m., 24%). The presence of *(86)* and phosphine oxide were confirmed by n.m.r.

The vacuum flash apparatus used in these experiments is described in detail in the experimental section.

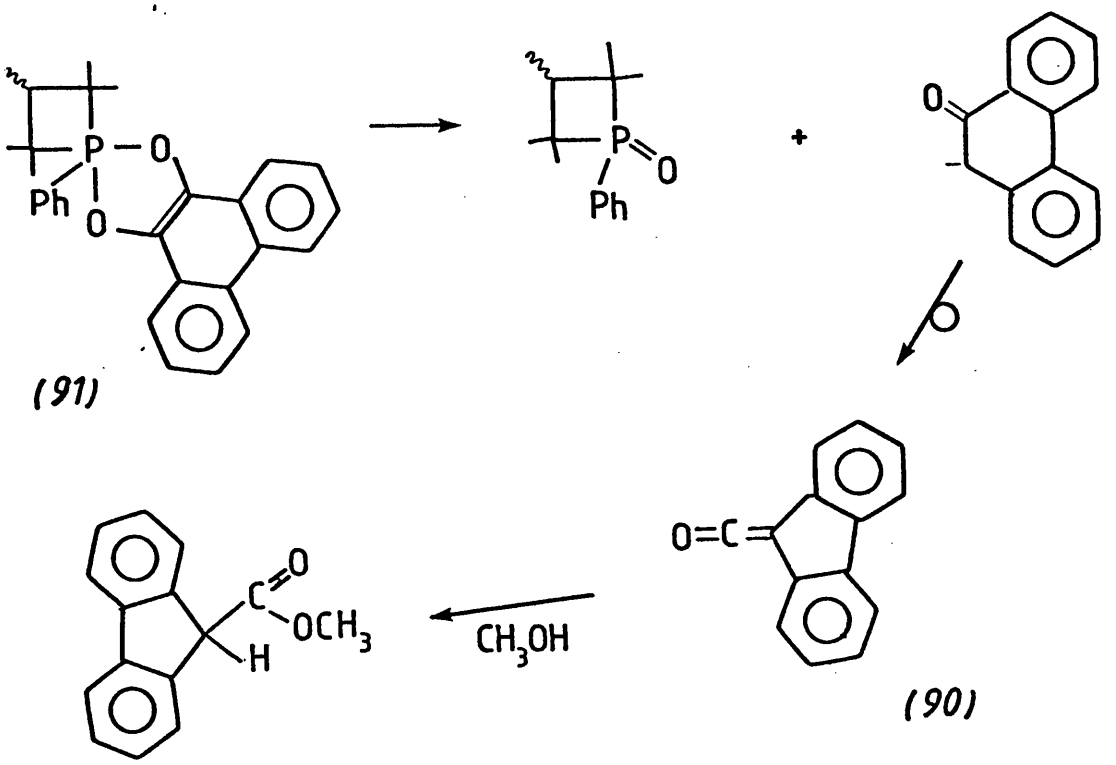
The results obtained showed as a general rule that both the P(III) compounds and the phosphoranes in which the group attached to the nitrogen atom was a methyl group are much more stable than the corresponding molecules in which a phenyl group is attached to nitrogen. When 2,3-diphenyl-1,3,2-oxazaphospholan is left at room temperature it polymerizes whereas 3-methyl-2-phenyl-1,3,2-oxazaphospholan does not. These differences in reactivity are directly related to the stability of the radical formed during these reactions, the phenyl group being able to stabilise the radical on the nitrogen atom while the methyl group would de-stabilise a similar species, Scheme 5.

SOME REACTIONS OF 1,3,2-DIOXAPHOSPHOLANS

A number of experiments were undertaken to try and use the phosphoranes *(91)* and *(92)* in the synthesis of the ketenes *(90)* and *(93)*. It was hoped that *(91)* and *(92)* would be cleaved into phosphine oxides and α-ketocarbanions. The former providing energy to make the reaction

more favourable while the latter rearranged into the ketenes.

Attempts to prepare the ketene *(90)* from the 2,2,3,4,4-pentamethyl-1-phenylphosphetan/9,10-phenanthraquinone adduct *(91)* by photolysis with u.v. light were unsuccessful.



(91)

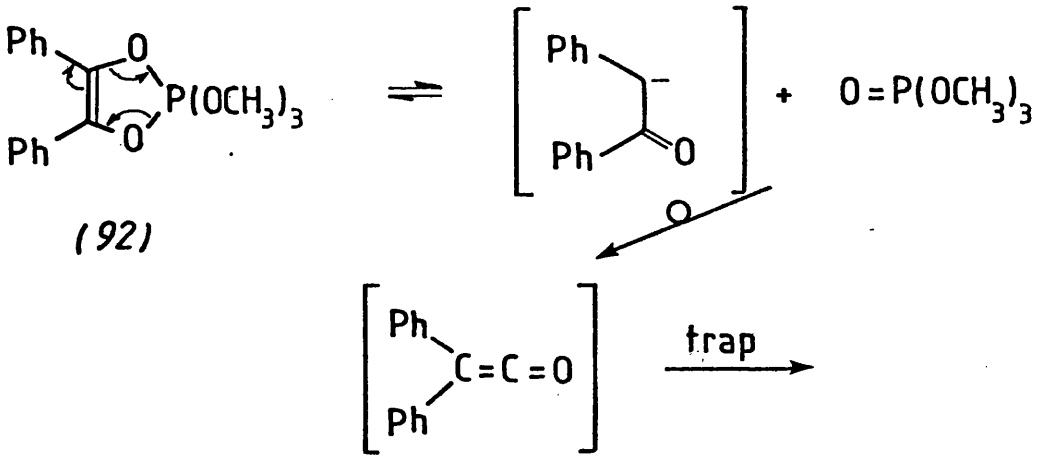
(90)

The ^{31}P n.m.r. spectrum of the photolysis mixture showed all the starting material to have been converted into a cis/trans mixture of 2,2,3,4,4-pentamethyl-1-phenyl-phosphetan 1-oxides; chromatography failed to isolate any other products.

The dark reaction of *(91)* in methanol gave unchanged starting material only. This suggested that the phosphetan oxides were derived photolytically rather than by hydrolysis and that the non-phosphorus containing product was either too polar to be extracted from a chromatography column or further decomposition occurred under these conditions.

Similar experiments using 4,5-diphenyl-2,2,2-trimethoxy-1,3,2-dioxaphosphol-3-ene *(92)* in an attempt to form diphenylketene *(93)*,

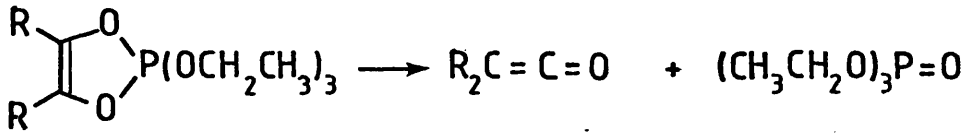
thermolytically, also failed to give the expected products.



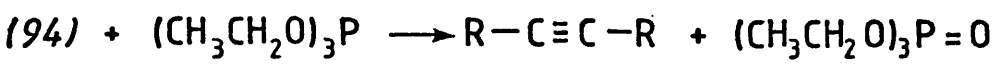
(92)

(93)

Mukaiyama [46] has shown that acetylenes *(95)* are formed when two moles of triethyl phosphite are reacted with one mole of an α-diketone. The mechanism of this reaction is thought to be formation of a diaryl or alkylaryl ketene *(94)* which is deoxygenated by the second mole of triethyl phosphite.



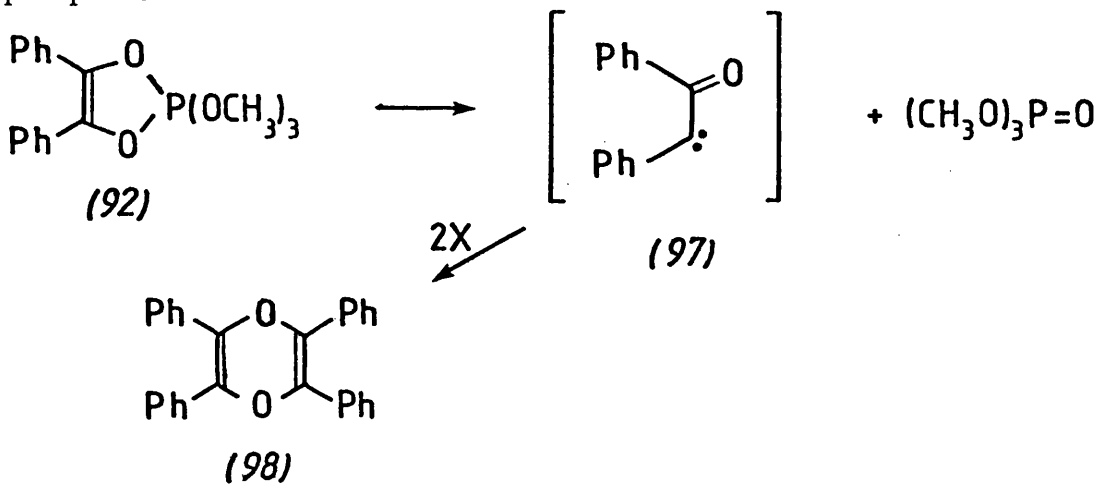
(96) (94)



(95)

When the trimethyl phosphite/benzil adduct *(92)* was thermolysed at 200°C for eighteen hours, the only products obtained were benzil and trimethyl phosphite. Chromatography of the reaction mixture isolated benzil and the hydrolysis products of trimethyl phosphite only. This adduct is much more unstable than the triethyl phosphite/benzil *(96)* compound and is more susceptible to breakdown to the component compounds.

When the adduct *(92)* was dissolved in methanol and the solution stored in the dark for three hours again benzil and trimethyl phosphite were formed. Photolysis with u.v. light ($\lambda = 254$ nm) gave the same products but also 2,3,5,6-tetraphenyl-1,4-oxe-2,5-diene *(98)*, as identified by its mass spectrum. This could have originated from the species *(97)*, which would also explain the formation of trimethyl phosphate.



The vacuum flash thermolysis of 4,5-diphenyl-2,2,2-trimethoxy-1,3,2-dioxaphosphol-3-ene *(92)* was attempted at two different temperatures. At 600°C the major products were the dissociation products, benzil and trimethyl phosphite, with two very minor peaks in the g.l.c. which appeared in the thermolysis at the higher temperature. At 750°C the products identified were benzil, trimethyl phosphite (57% of the phosphorus containing material) and methyl dimethylphosphinate (43% of the phosphorus containing material), probably formed by an Arbuzov rearrangement of trimethyl phosphite.

The results of the above experiments have shown that the phosphoranes investigated while appearing to decompose thermally and photolytically, the products obtained are difficult to isolate.

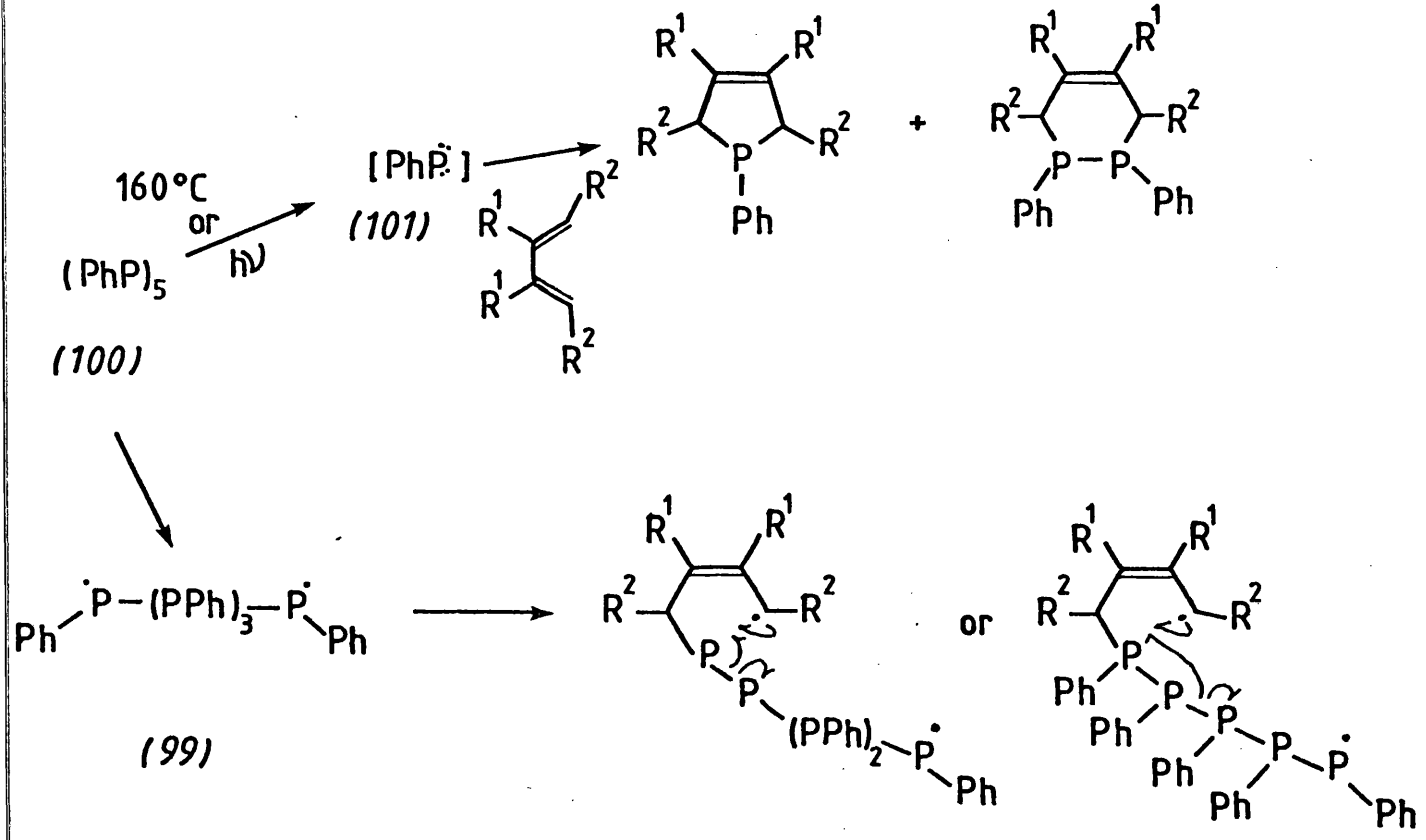
CHAPTER TWO

CHAPTER TWO

SOME REACTIVE PHOSPHORUS INTERMEDIATES

(i) Phenylphosphinidene (Ph-P)

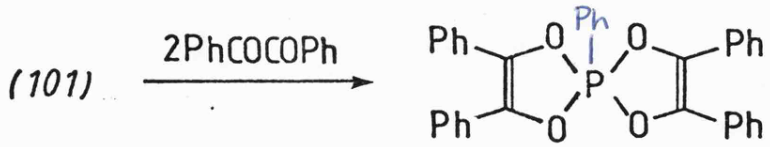
Schmidt and Boie [52] have reported that thermal decomposition or photolysis of pentaphenylcyclopentaphosphine *(100)* in the presence of 1,3-dienes gives cyclic compounds, the formation of which can be interpreted as attack of phenylphosphinidene *(101)* or a diradical *(99)* upon the 1,3-dienes as shown by Scheme 6.



SCHEME 6

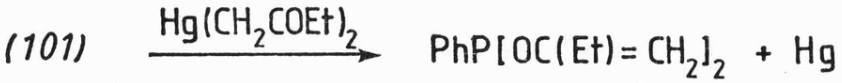
Phenylphosphinidene *(101)* has also been reported to be formed in a number of other ways, for example, the reaction of zinc with phenylphosphorus dichloride and the reaction of iodine upon phenylphosphine,

although both these reactions have poor yields of the trapped form of *(101)*.

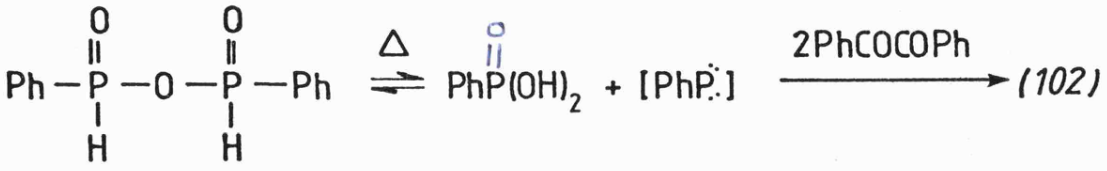


(102)

(103)



The phenylphosphinidene species has been trapped in a number of reactions [53]. It reacts with benzil to form the phosphorane *(102)* and with diethyl disulphide to form diethyl phenylthiophosphonite *(103)*. The thermal decomposition of phenylphosphinic anhydride *(104)* [54] may lead to the formation of phenylphosphinidene since in the presence of benzil the phosphorane *(102)* is again formed, phenylphosphonous acid *(105)* being the other product.



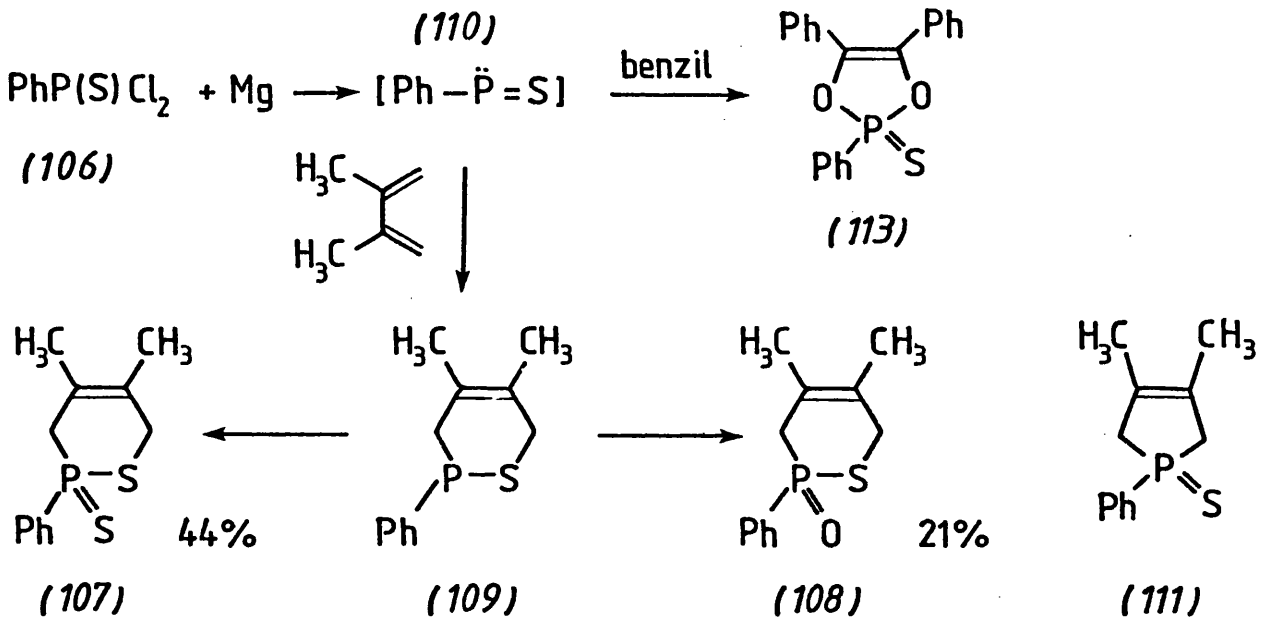
(104) *(105)*

(ii) Phenylphosphinothioylidene *(110)*

When phenylphosphinothioic dichloride *(106)* is dechlorinated with magnesium [56] in tetrahydrofuran in the presence of 2,3-dimethylbuta-1,3-diene at 50°C, 4,5-dimethyl-2-phenyl-3,6-dihydro-1,2-thiaphosphorin 2-sulphide *(107)* and the corresponding 2-oxide *(108)* are obtained. These products can be rationalized as being formed by the oxidation of

(109) to give *(108)* and the sulphurization of *(109)* by *(106)* to give *(107)*. It seems reasonable that *(109)* is formed via a Diels-Alder type reaction of phenylphosphinothioylidene *(110)* as a 1,2-dipole, and the diene. Similar reactions occur between dienes and thionitroso compounds [55]. An expected product *(111)* in the above reaction was not isolated.

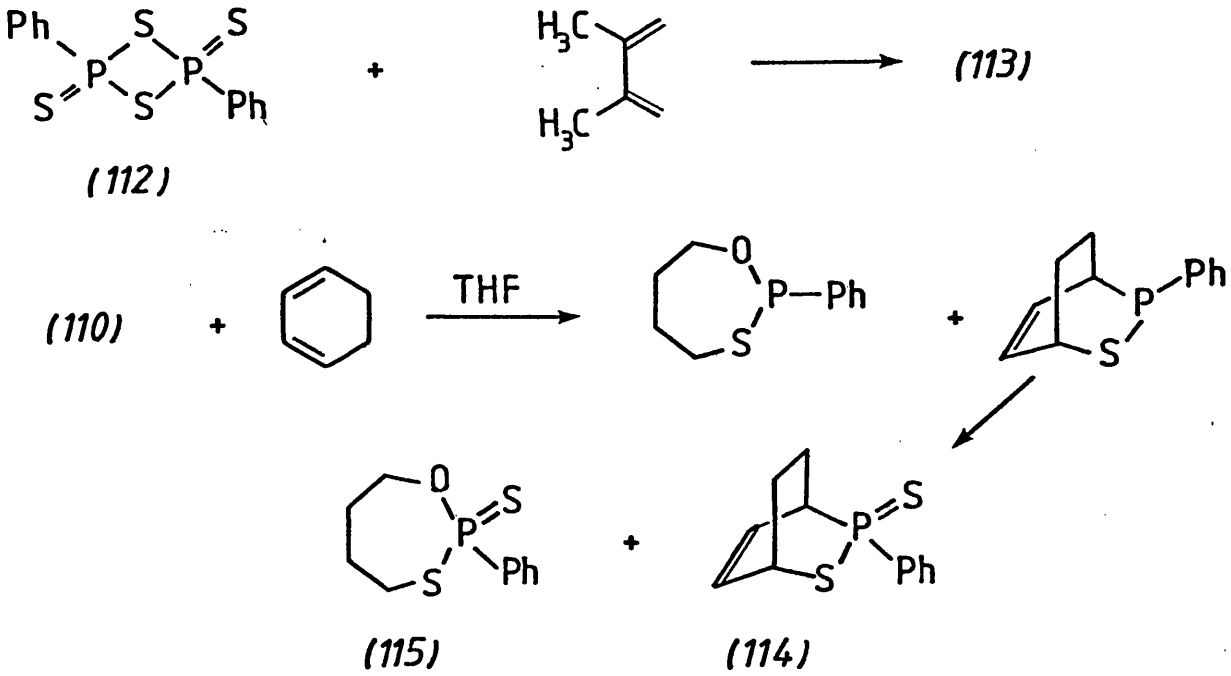
Nakayama has shown [57] that phenylphosphinothioylidene *(110)* can be trapped with benzil to give 2,4,5-triphenyl-1,3,2-dioxaphosphol-3-ene 2-sulphide *(113)*.



Compound *(113)* was also the product in the reaction of 2,3-dimethyl-buta-1,3-diene and the dimer *(112)*; again the proposed intermediate is phenylphosphinothioylidene [57].

Similar reactions are described in which cyclohexa-1,3-diene is used as the trapping agent [56].

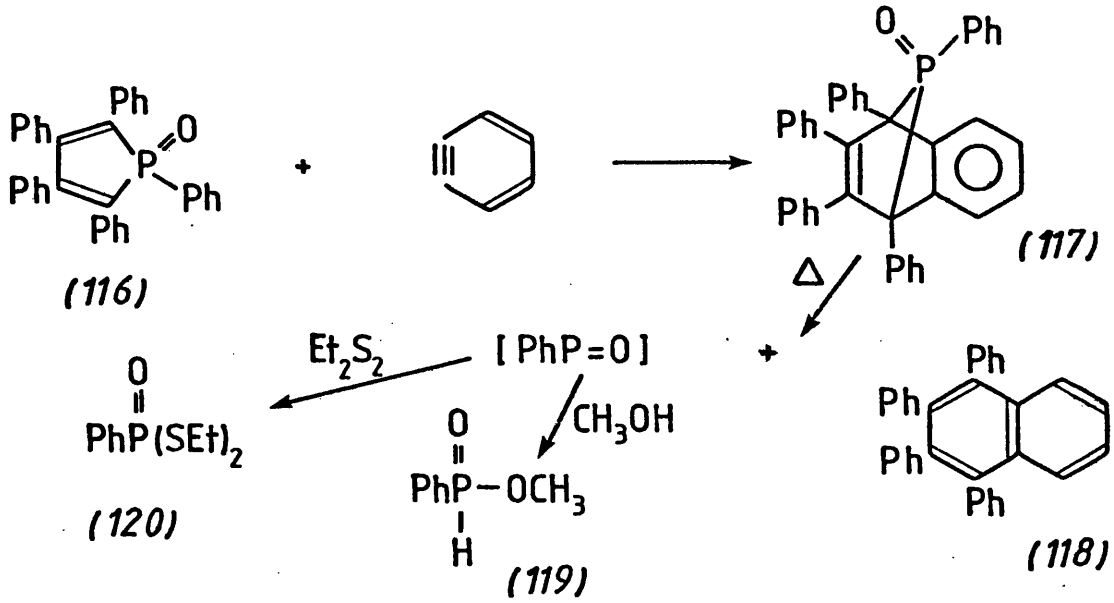
The products obtained not only include the expected 1,4-addition product, 6-phenyl-5-thiaphosphabicyclo-[2.2.2]-oct-2-ene 6-sulphide *(114)* but also a product from the reaction of the phosphinothioylidene and the solvent, that is 2-phenyl-1,3,2-oxathiaphosphepane 2-sulphide *(115)*, formed by insertion into the C-O bond of THF.



(112) (113) (110) (115) (114)

(iii) Phenylphosphinylidene

1,2,3,4,5-Pentaphenylphosphole 1-oxide *(116)* reacts with benzyne [58] to form the bicyclic oxide *(117)*. Upon heating, this molecule decomposes to form tetraphenylnaphthalene *(118)*.

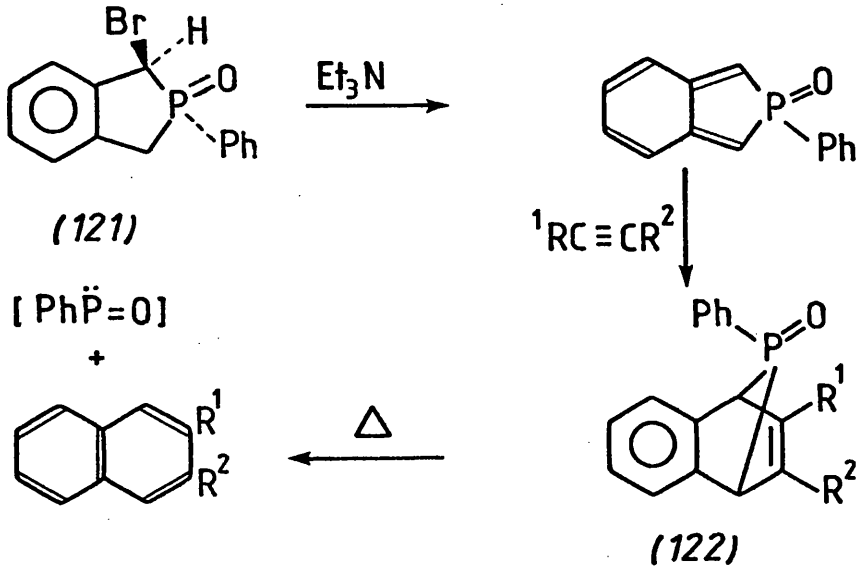


(116) (117) (118) (119) (120)

In the presence of methanol methyl phenylphosphinate *(119)* is also formed; if, however, diethyl disulphide is present then the species obtained is diethyl phenylthiophosphonate *(120)*, the products being explained as formation of *(117)* which cleaves phenyl phosphinylidene

thereby aromatizing the rest of the molecule giving a substituted naphthalene, the reactive phosphinylidene is trapped by either methanol or diethyl disulphide. Interestingly, the phosphole oxide cannot be trapped by either isoprene or acetylene.

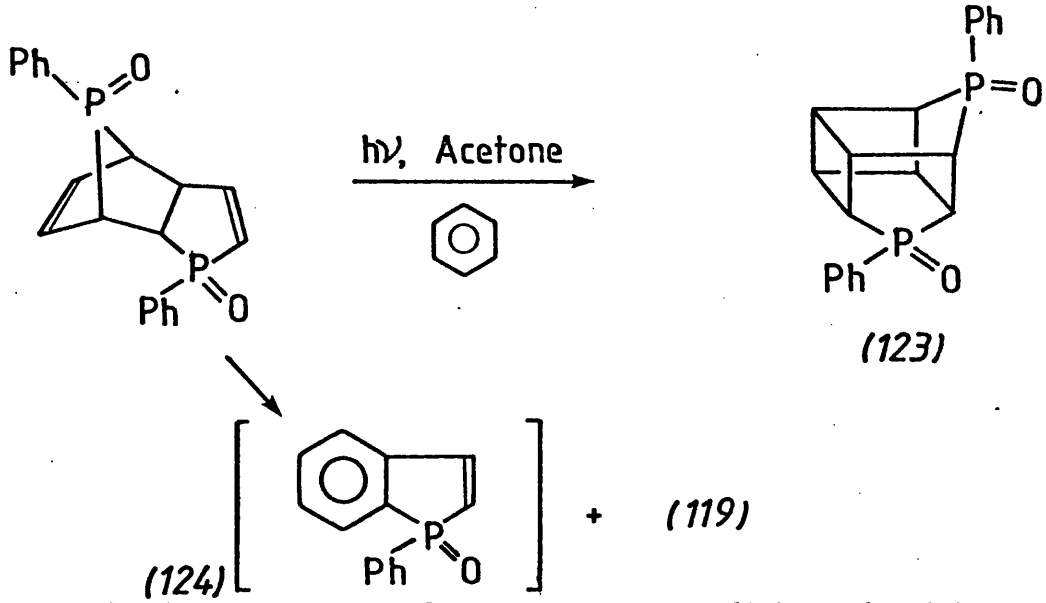
A related reaction [59] occurs when 1-bromo-4,5-benzo-2-phenyl-phosphol-3-ene 2-oxide *(121)* is treated with triethylamine. The resultant phosphole can be trapped with acetylenes to give a bicyclic phosphine oxide *(122)*. This undergoes the same type of cleavage reaction as *(117)* giving similar products.



Other phospholes can also be trapped by dienophiles to give bridged bicyclic oxides, 1,2,5-triphenylphosphole 1-oxide for example [60]. Again, heat causes the formation of a substituted naphthalene and, presumably, phenylphosphinylidene.

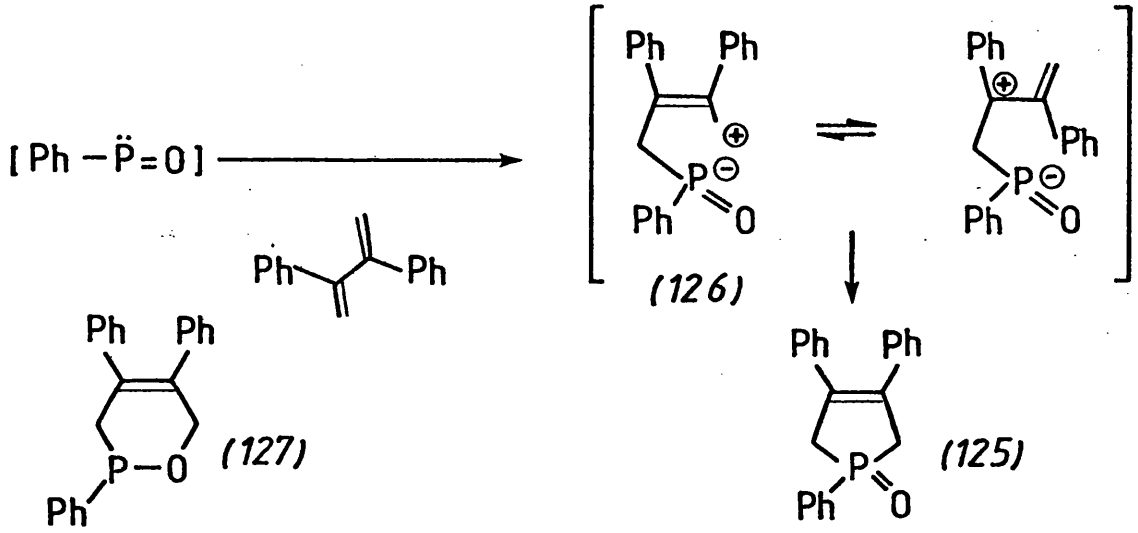
Japanese workers [61] have shown that the dimer of 1-phenyl-phospholen 1-oxide can undergo two different types of photochemical reactions, the products formed depending upon the conditions, the reaction in benzene-acetone giving a caged cis-oxide via a photo-reduction of the double bonds. Reaction in methanol affords methyl phenylphosphinate *(119)* and a phosphindole oxide *(124)* which was not

isolated. The fragmentation reaction successfully competes with the reduction in methanol.

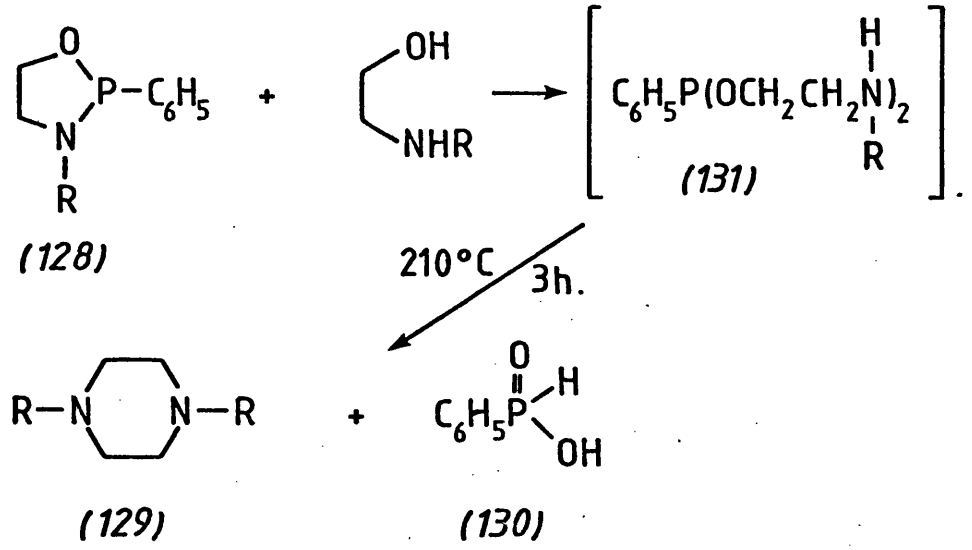


Finally, the dechlorination of phenylphosphonic dichloride with magnesium [56] in THF in the presence of 2,3-diphenylbuta-1,3-diene gives slightly different results to the reaction involving the sulphur analogue. The product obtained was 1,3,4-triphenylphosphol-3-ene 1-oxide *(125)*. This reaction is interesting in two ways, firstly, no six-membered ring compound was formed and, secondly, the reaction takes place with transoid 2,3-diphenylbuta-1,3-diene. The mechanism for the reaction involves electrophilic attack on the transoid 2,3-diphenyl-buta-1,3-diene by the phosphorus atom of phenyl phosphinylidene. A transoid Zwitterion *(126)* will be formed, which must convert into the cisoid Zwitterion and ring close to give *(125)*. The authors suggest *(125)* is formed preferentially to *(127)* because the P=O bond is stronger than the P=S bond and sulphur is more nucleophilic than oxygen.

1,3,2-Oxazaphospholans *(128)* have been shown to react with a mole of an aminoethanol to form 1,4-disubstituted piperazines *(129)* and phenylphosphinic acid *(130)* [62]. The reaction proceeds not via a



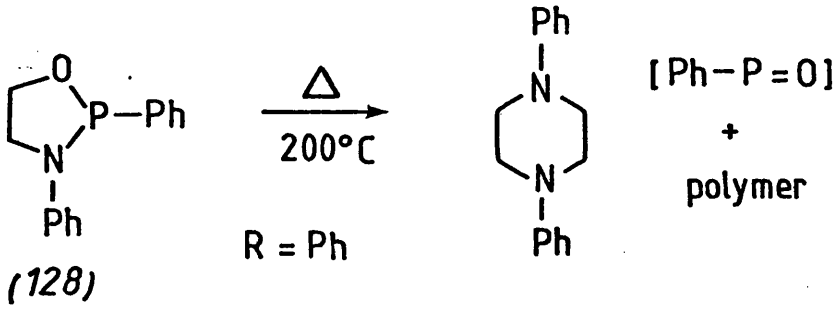
phosphorane but by ring opening of the oxazaphospholan ring upon the addition of the second mole of aminoethanol, the P(III) species *(131)* is formed, which on heating decomposes to the products. If the reaction had gone via a phosphorane then, as well as piperazine, 2-phenyl-1,3,2-oxazaphospholan 2-oxide would have resulted.



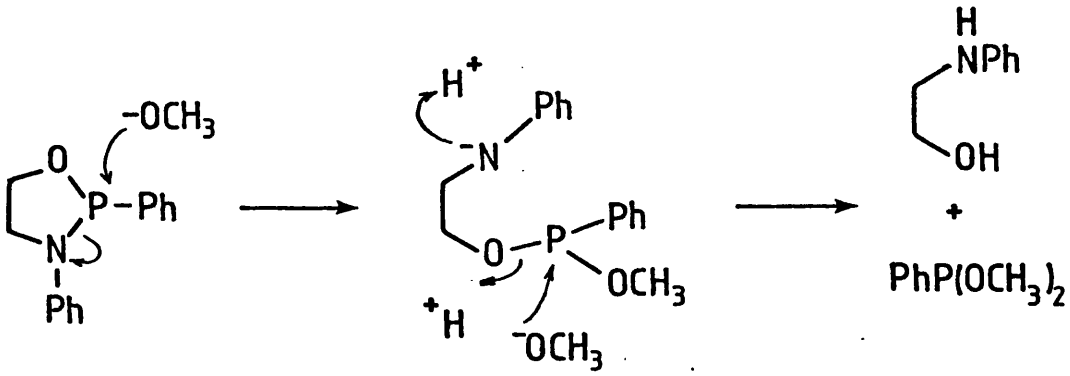
Some further reactions of 1,3,2-oxazaphospholans

During the preparation of *(85)* it was necessary to attempt a distillation of 2,3-diphenyl-1,3,2-oxazaphospholan *(128* R = Ph*)*; this led to its decomposition and formation of 1,4-diphenylpiperazine *(129* R = Ph*)* which was identified by its melting point and by its ^{1}H n.m.r. spectrum. This being the case then the other moiety formed must have been phenylphosphinylidene. Such a species, as has already been

mentioned, is highly reactive and presumably polymerized under the reaction conditions used.

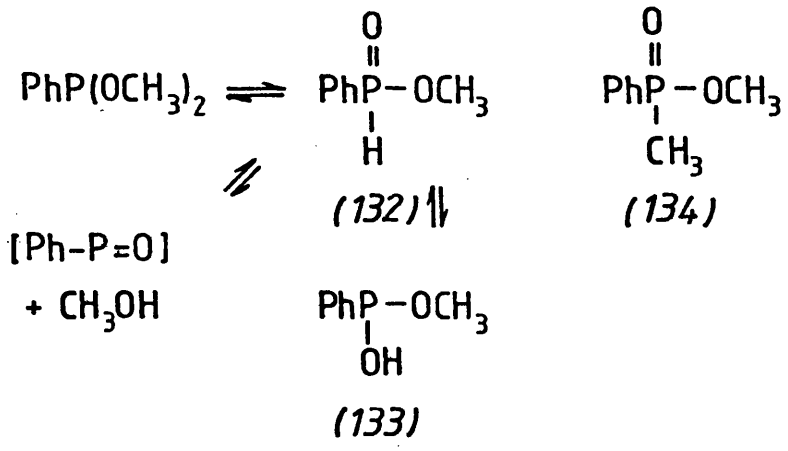


The basis of the work in this chapter was variation of the reaction conditions to detect phenylphosphinylidene using a suitable trapping reagent. The oxazaphospholan *(128)* reacted, not surprisingly, with methanol in the dark to give dimethyl phenylphosphonite, after two days. A small amount of what could have been methyl phenylphosphinate was also formed.



Photolysis of *(128)* in methanol for two hours showed the major product to be methyl phenylphosphinate *(132)*, which was identified by the P-H peaks in the ^{1}H n.m.r. spectrum and the larger doublet in the coupled ^{31}P n.m.r. spectrum. The formation of this compound is readily explained in terms of addition of methanol to a molecule of phenylphosphinylidene.

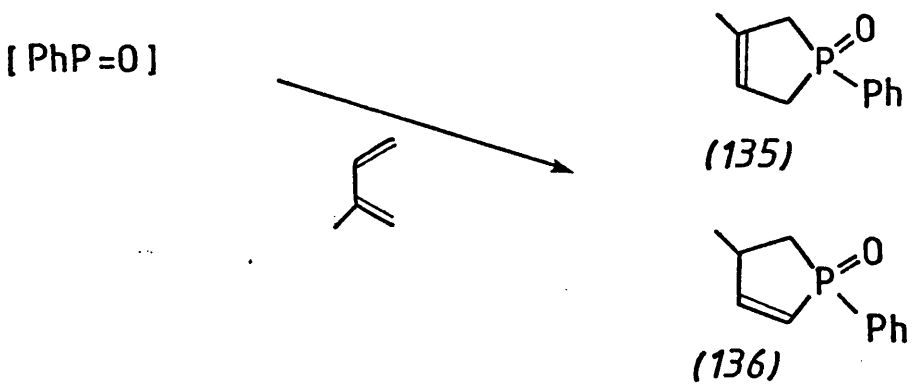
The evidence from the ^{31}P n.m.r. of the dark reaction of *(128)* (R = Ph) in methanol showed dimethyl phenylphosphonite as the major



product (93%) and methyl phenylphosphinate as a minor product (7%). This suggests that in the photolysis dimethyl phenylphosphinate is formed initially and this is subsequently hydrolysed to *(133)* before rearranging to *(132)*. If it were to rearrange before hydrolysis then *(134)* would be generated and the replacing of the methyl group by a hydrogen atom does not seem too probable. These results suggest two mechanisms are running concurrently, some oxazaphospholan is reacting with the solvent (probably a slow reaction) but some is also undergoing a photochemical reaction and it seems likely that phenylphosphinylidene is formed.

An attempt was made to photolyse the 1,3,2-oxazaphospholan in another solvent. Acetonitrile was chosen because it was found only starting material was obtained in the dark reaction, isoprene was added as a trap so that if phenylphosphinylidene was produced in the reaction mixture it would have reacted with it to give either 3-methyl-phosphol-3-ene 1-oxide *(135)*, or 4-methyl-1-phenyl-phosphol-2-ene 1-oxide *(136)*. Although in this reaction *(135)* would be formed initially, phosphol-3-enes are known to isomerise to phosphol-2-enes because of the energy gained in placing the double bond in conjugation with the phosphorus atom, thus *(136)* might also be expected as a product.

Photolysis for two hours produced neither of the expected products

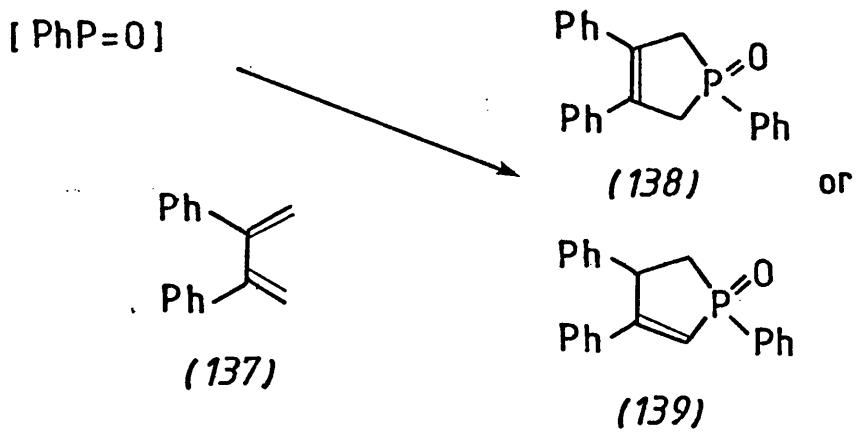


but mainly unreacted starting material and its oxide, plus three minor peaks. Photolysis for a longer period (eighteen hours) gave oxide and two other peaks, ^{31}P n.m.r. -26 p.p.m. and -16 p.p.m. An attempt to separate out the products by thick-layer chromatography gave 43% of a substance with a ^{31}P n.m.r. value of -19 p.p.m. This substance appears to be an hydrolysis product as a colour change was observed when the samples were adsorbed onto the t.l.c. plates.

As the trapping experiments in acetonitrile failed to produce evidence of phenylphosphinylidene, the reaction conditions were changed. Photolysis was performed in dichloromethane with 2,3-diphenylbuta-1,3-diene *(137)* as the trapping reagent.

Again the expected products are phospholenes; these were 1,3,4-triphenyl-phosphol-3-ene 1-oxide *(138)* and 1,3,4-triphenyl-phosphol-2-ene 1-oxide *(139)*, again *(139)* resulting from isomerisation of *(138)* to bring the double bond in conjugation with the phosphorus atom. The only product observed was at -19 p.p.m. in the ^{31}P n.m.r. spectrum, and this seems likely again to be the hydrolysis product, as this ^{31}P value is very similar to the products obtained in the earlier reactions after attempts to purify the products by column chromatography.

When 2,3-diphenyl-1,3,2-oxazaphospholan was heated under nitrogen in the presence of 2,3-diphenylbuta-1,3-diene and o-dichlorobenzene (50 ml) at reflux temperature for eight hours, the only products



observed in the ^{31}P n.m.r. spectrum were 2,3-diphenyl-1,3,2-oxaphospholan 2-oxide and unreacted starting material. When the reaction was repeated using less o-dichlorobenzene and heating at 190°C for three-and-a-half hours the ^{31}P n.m.r. spectrum gave a peak at -15 p.p.m. These products were not the expected results and probably result from hydrolysis, oxidation, or in the latter case polymerization of the phenylphosphinylidene species.

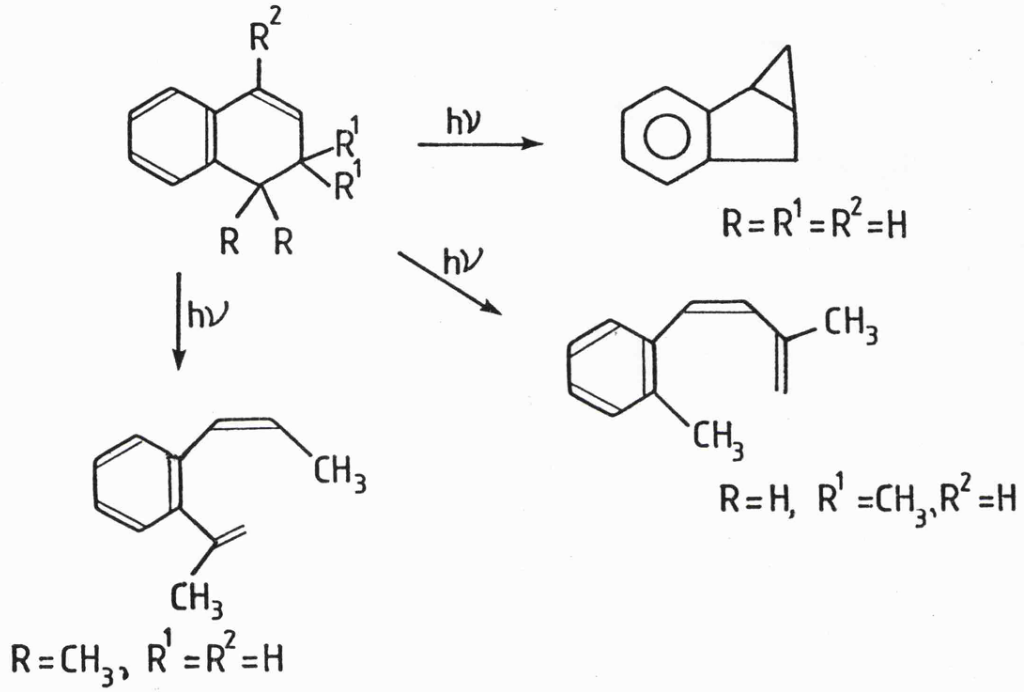
Using vacuum flash thermolysis similar results were obtained, when the furnace was at 800°C. This suggests that if phenylphosphinylidene had been formed in any of these reactions it must be in an excited state and quickly polymerizes before it can be trapped out.

CHAPTER THREE

CHAPTER THREE

THE PREPARATION AND PHOTOLYSIS OF DIHYDROPHOSPHINOLINES

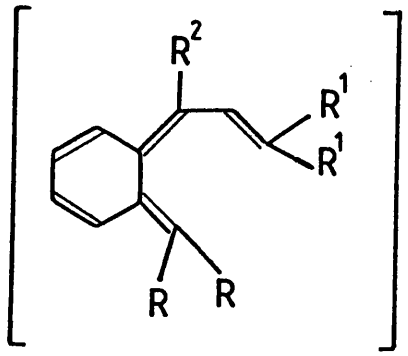
Alkyl-substituted - 1,2-dihydronaphthalenes when irradiated with a low pressure mercury lamp, have been shown [63,64] to undergo electrocyclic ring opening reactions to yield substituted-allenyl-benzenes, Scheme 7, and cyclopropane species.



SCHEME 7

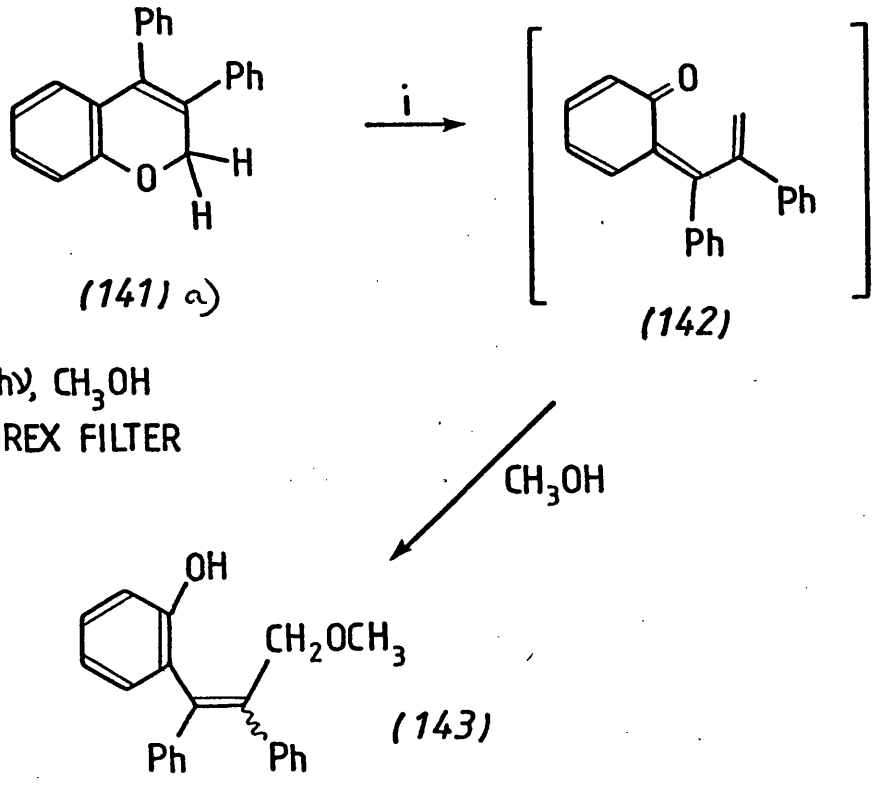
The intermediate in these reactions is thought to be the o-quinodimethane *(140)*. Irradiation at -180°C in a matrix of 2,2-dimethylbutane/pentane gave rise to a u.v. maximum at 402 nm which was assigned to this species.

Work by Padwa [65] on the irradiation of chromenes *(141)* and isochromenes has shown similar results to the above, the reaction (of (141a)) in methanol going via the intermediate *(142)*, which forms a [1,6]-methanol



(140)

adduct to give the methyl ether *(143)*, the absence of a [1,4]-methanol adduct was rationalized as showing steric hindrance in the intermediate. The corresponding isochromene system *(144)* yields indene epoxide *(145)* as the major product, via an o-quinoidal species, 1-methoxy-1,2-diphenylindan-2-ol *(146)* being a secondary photolysis product formed from the indene epoxide *(145)*. The difference in products obtained by the photolysis of isochromene and chromene rings has been attributed to the variation in reactivity of the o-quinoidal intermediates. Michael addition of methanol to the labile o-quinoidal



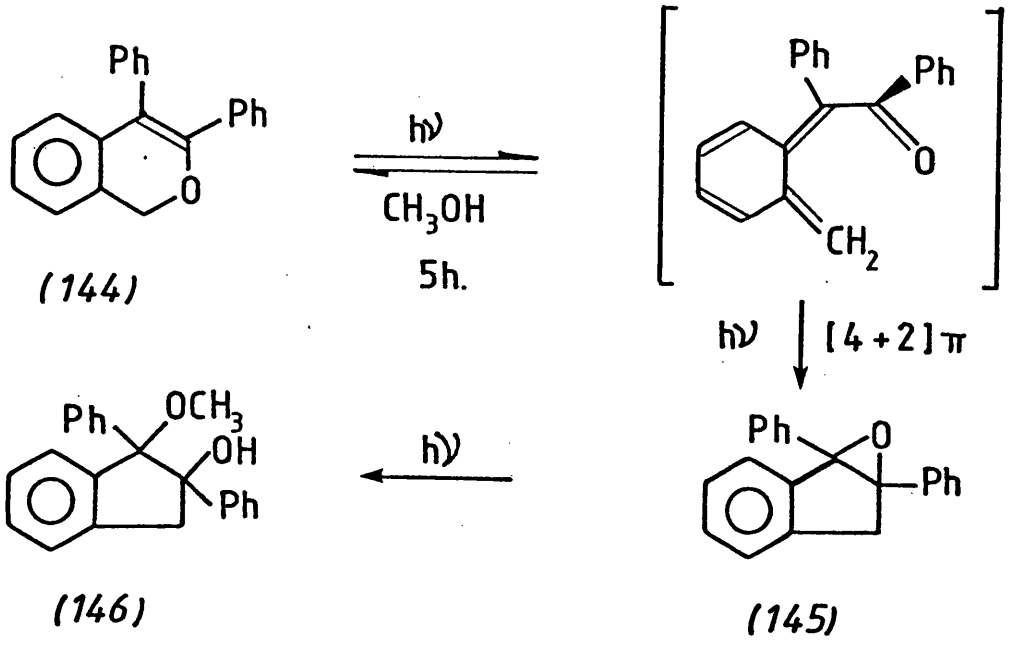
(141) a)

(142)

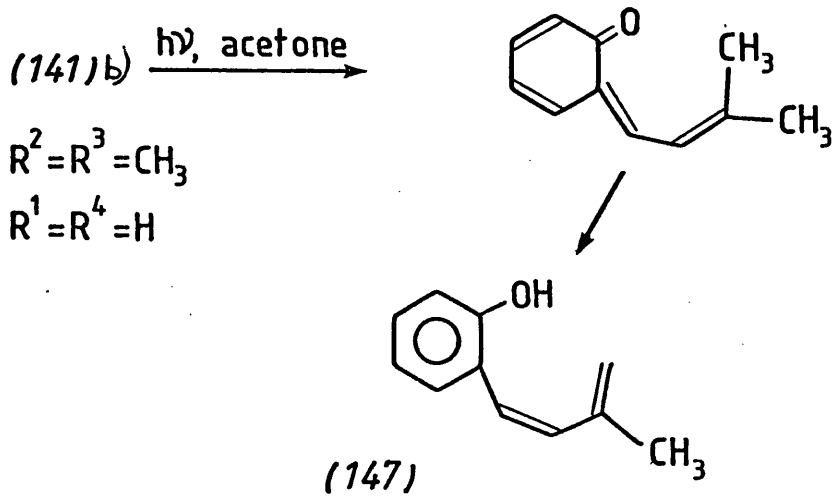
i. hν, CH_3OH
COREX FILTER

CH_3OH

(143)

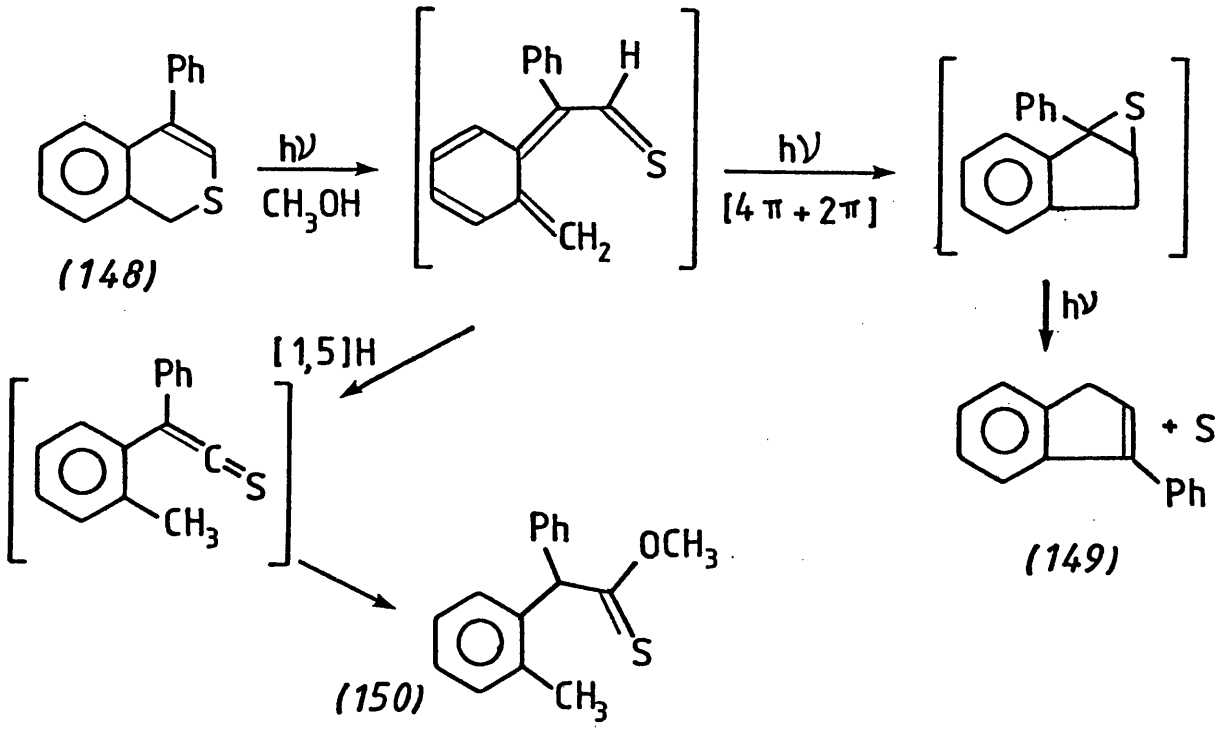


moiety produced from the 2H-chromene system would be expected to occur quite readily. This facile conjugate addition destroys the necessary chromophore for the subsequent $4\pi + 2\pi$ photo-cycloaddition reaction. Attack by methanol on the o-quinoidal intermediate obtained from the isochromene system is not as rapid and consequently this species is long lived enough to absorb another photon of light and undergo an intramolecular photo-cycloaddition reaction.



Photolysis of *(141)* $R^2 = R^3 = CH_3$, $R^1 = R^4 = H$ in an inert solvent such as acetone leads to the phenol *(147)*; corresponding to a photoinduced [1,7]-sigmatropic hydrogen shift.

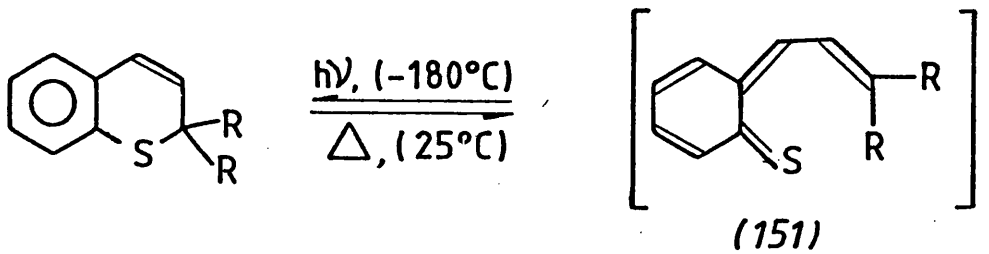
Padwa [65] has also reported the photolysis of the isothiochromene *(148)*. This is seen to undergo similar electrocyclic reactions, to give 3-phenylindene *(149)*, the thio-methyl ester *(150)* and elemental sulphur. Further evidence for the intermediates of all these types of irradiation reactions comes from Kolc and Becker [66-69]. Their work involves low temperature rigid-matrix irradiations which produce photochromic effects, in which a green intermediate *(151)* is observed.



(148)

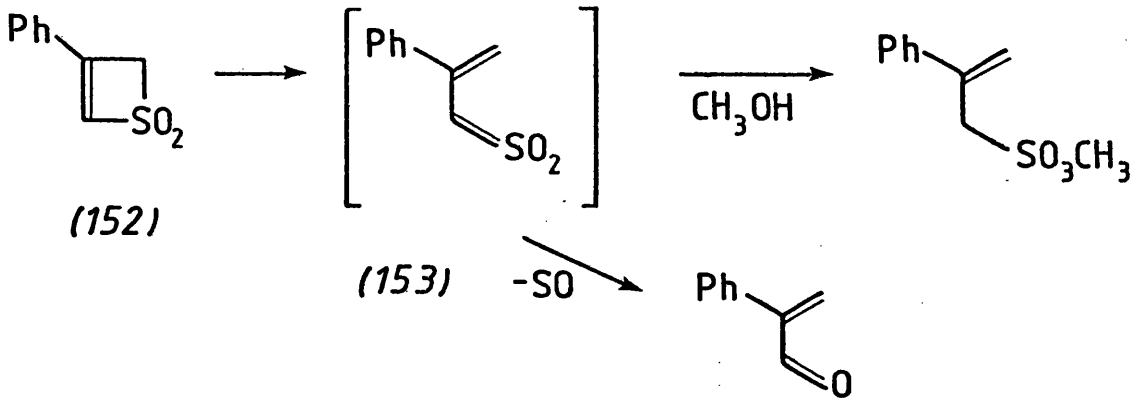
(149)

(150)

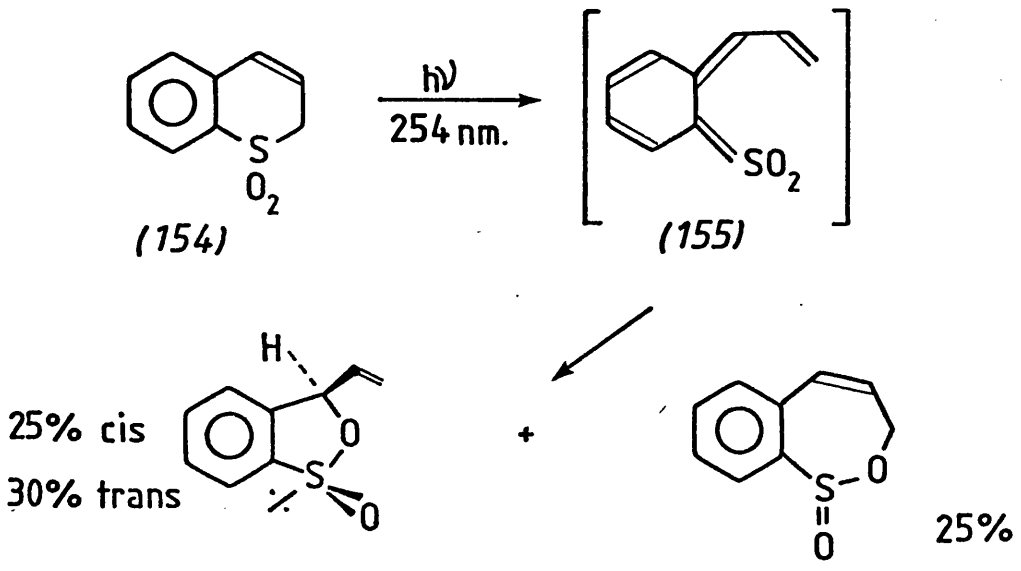


(151)

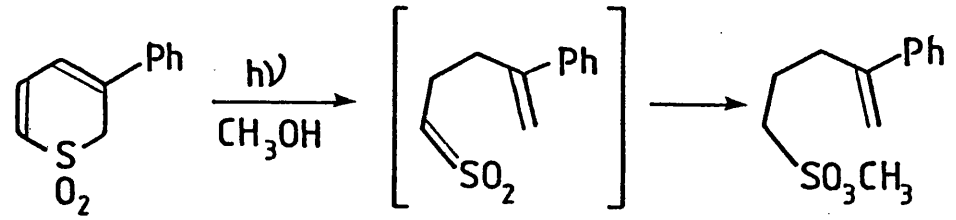
Sulphene intermediates [73] have been proposed in the photolytic [71,72] and thermolytic [70] fragmentations of cyclic sulphones. Thiete sulphone derivatives *(152)* photolyse via the vinyl sulphenes *(153)* to give the products shown.



The photolysis of 2H-1-benzothiopyran-1,1-dioxide *(154)* in methanol [74] (or dichloromethane) gave a mixture of cyclic sulphinate esters (sultines). The intermediate *(155)* was not trapped by either methanol or reactive dienophiles. This was rationalized as a rapid return to aromatization of the sulphene upon formation.

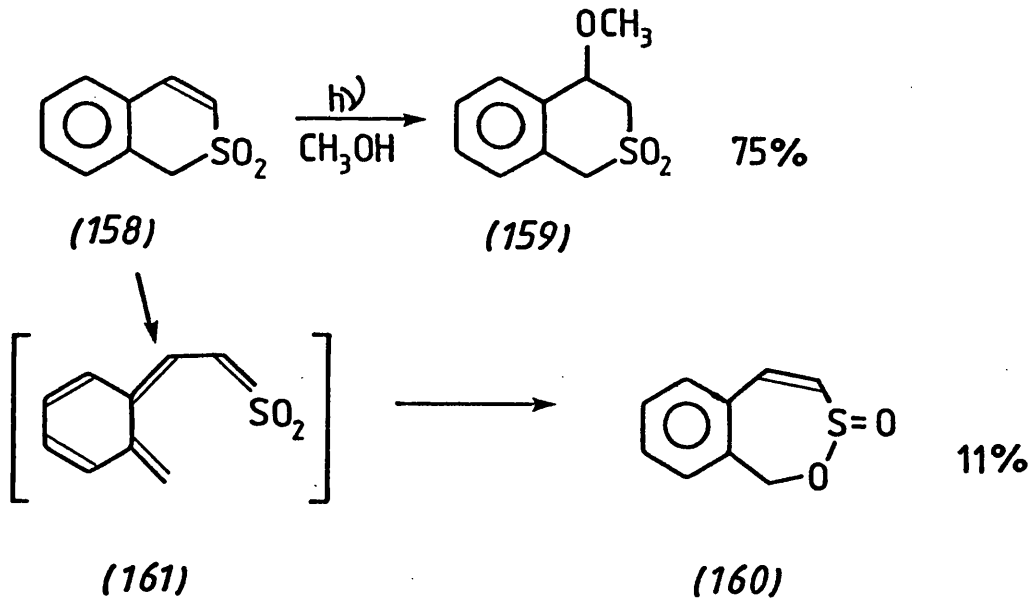


The sulphene intermediate postulated was supported by work of King [73] who had shown that the sulphinate ester *(156)* was obtained from the irradiation in methanol of the sulphone *(157)*.



(157) *(156)*

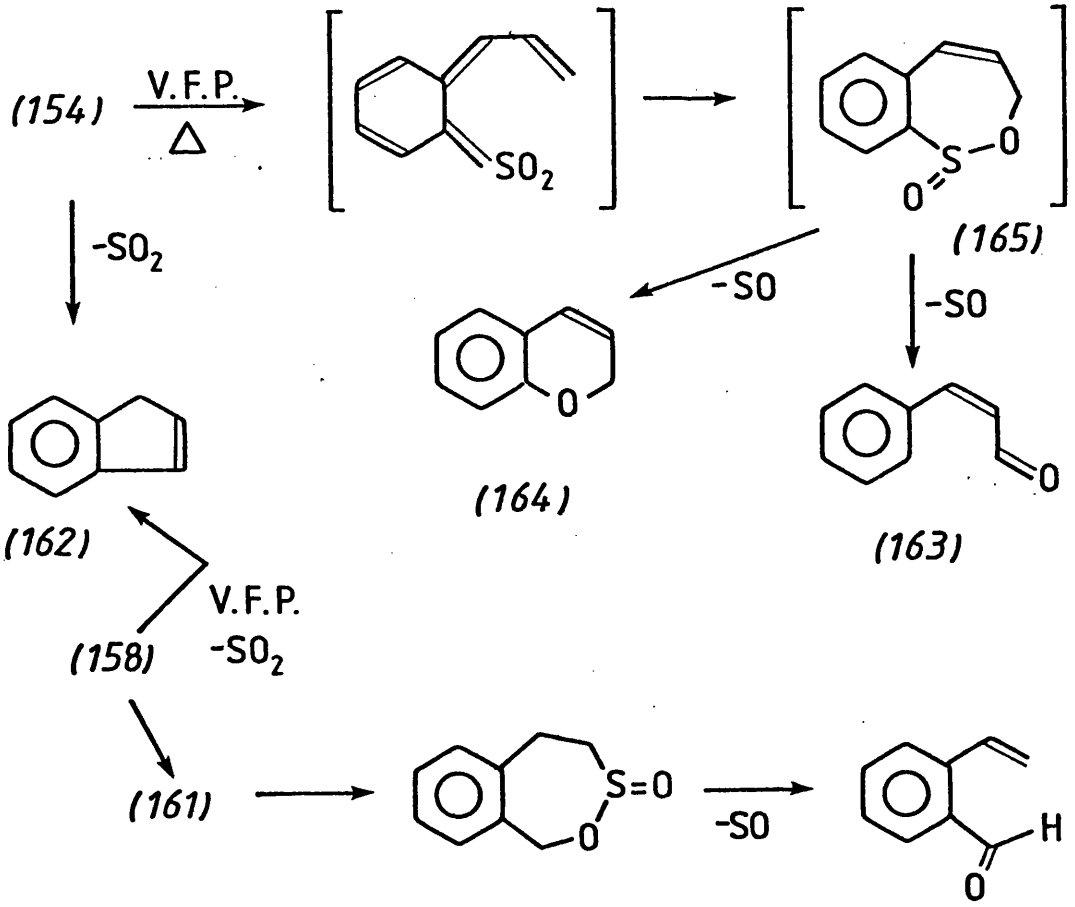
The reaction of 1H-2-benzothiopyran-2,2-dioxide *(158)* under these conditions gives the unusual product *(159)* and only a small amount of *(160)*, which was obtained by the ring-opening of *(158)* to give *(161)* then ring-closure to incorporate an oxygen atom.



(158) *(159)*

(161) *(160)*

Finlay has shown [75] that *(154)* undergoes a thermal electrocyclic ring-opening reaction, producing indene *(162)*, cinnamaldehyde *(163)*, and 2H-1-benzopyran *(164)*.

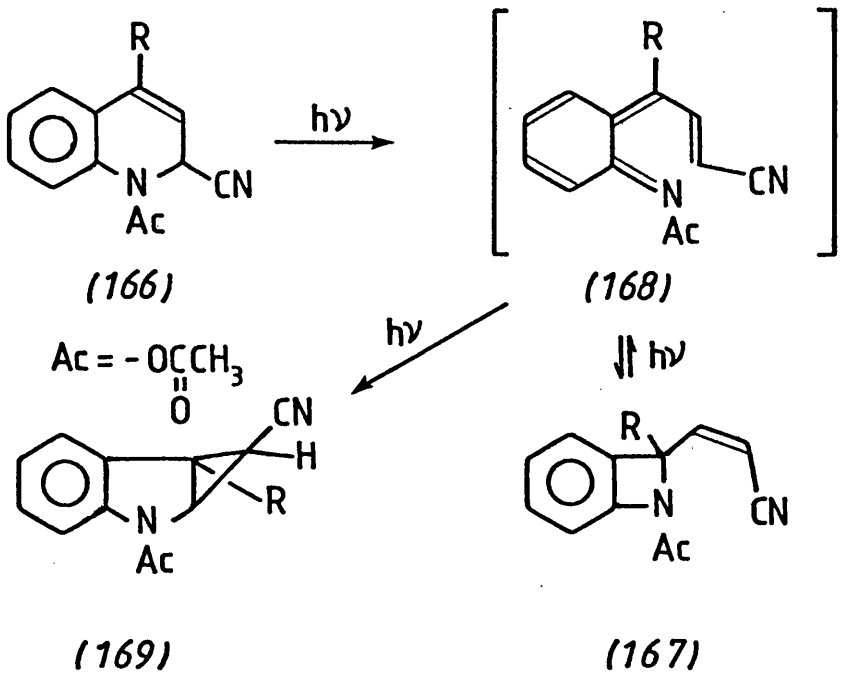


The indene was obtained by a direct extrusion of sulphur dioxide from *(154)*, while the products *(163)* and *(164)* were formed from the sultine *(165)* which loses sulphur monoxide. Vacuum flash pyrolysis of 1H-2-benzothiopyran *(158)* also gave indene, and another product, o-vinylbenzaldehyde.

Since cinnamaldehyde produced from the thermolysis of *(154)* could have resulted from a rearrangement of 2H-1-benzopyran *(164)*, under the reaction conditions, it was thermolysed [75]. The products obtained by V.F.P. at 850°C were a mixture of cinnamaldehyde (13%), 4H-1-benzopyran (34%) and unchanged starting material (52%). The suggestion was made that this reaction had proceeded via an initial diradical which underwent a [1,5]-H shift and collapsed to give *(163)*, the 4H-1-benzopyran resulting from a [1,3]-H transfer, although a supra-facial

migration would be thermally symmetry forbidden.

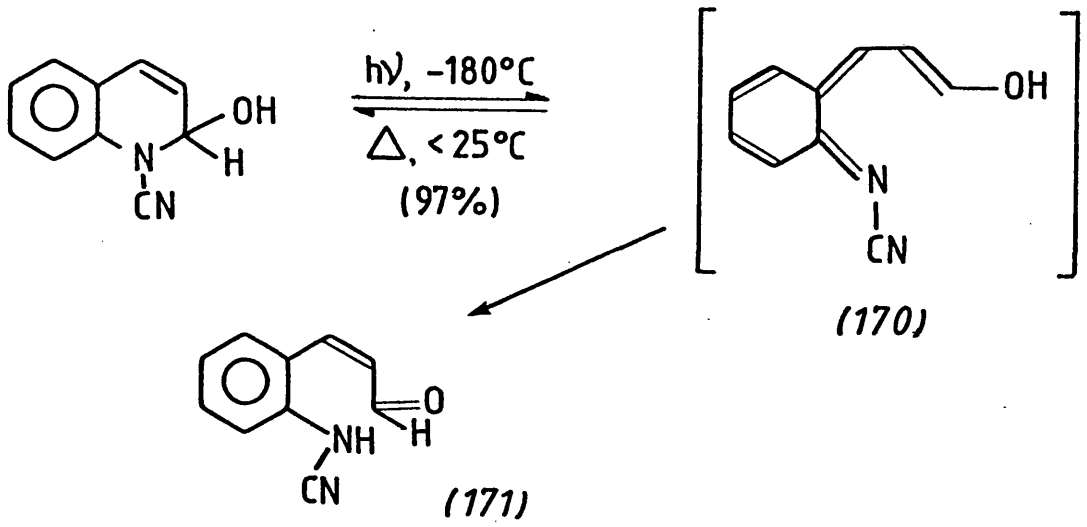
1-Acetyl-2-cyano[1,2]-dihydroquinolines *(166)* isomerize photochemically to form the N-acetylbenzoazetines *(167)* [76].



Irradiation in ethanol (or ether) with a 350 watt high pressure lamp (pyrex filter) gave *(167)* and *(169)*, the relative yields depending upon the period of irradiation and the solvent. The longer the irradiation time the greater the proportion of *(169)* obtained (hv, ten hours, *(169)* is 100%). This suggests the presence of a benzoazahexatriene intermediate which undergoes a fast and reversible isomerization to *(167)* (this was the major product up to a three hours photolysis) which undergoes a slow and irreversible isomerization to *(169)*.

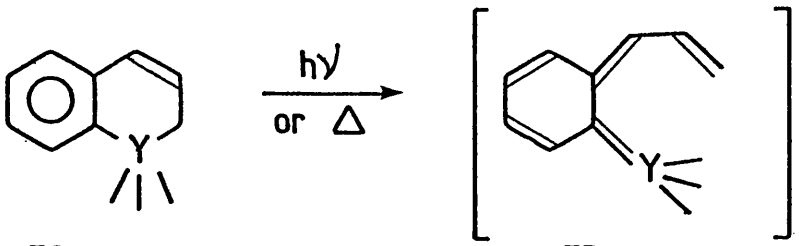
A similar reaction was observed in the work of Kolc and Becker [69], where the intermediate *(170)* reverts back to starting material at the rate of 97% per cycle, that is, after every irradiation 97% of the starting material is recovered and 3% converted into *(171)*. It seems

reasonable from the above evidence that, in general, systems of the type *(172)* can undergo electrocyclic ring opening by the effect of heat or light to form the general intermediate *(173)*; similarly *(174)* can be transformed into *(175)*.

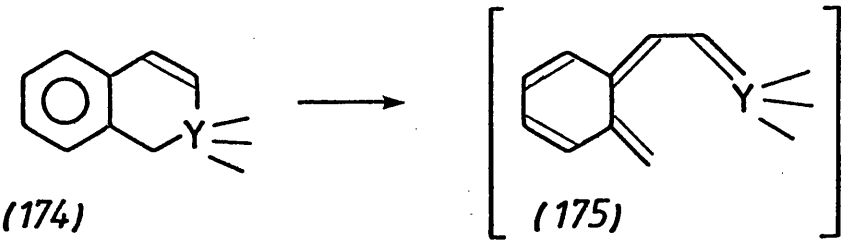


These species may then do one of three things: (i) return to the starting material, (ii) rearrange intramolecularly and/or (iii) be trapped. So far (iii) has only been achieved by solvolysis. This scheme has been applied to molecules in which Y = C, O, N or S. The following work shows that it can also be applied when Y is equal to phosphorus.

The first thing to consider is how to prepare carbon-phosphorus heterocycles containing six-membered rings, that is phosphinolines, in sufficient yields to carry out further work.



(172) (173)

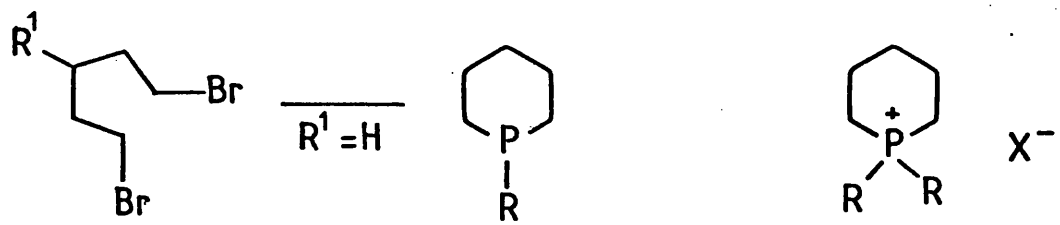


(174) (175)

THE SYNTHESIS OF PHOSPHINOLINES AND RELATED MOLECULES

Phosphorinans and Phosphorindienes

By far the largest group of preparative routes to phosphorinans involve the cyclisation of 1,5-dibromopentane *(176)* [77]. Gruttner was the first to successfully do this using Grignard reagents and an arylphosphinous dichloride [78]. Later methods include use of di-lithium alkyl phosphorins [80] and tributyl phosphite [79] which gives the oxide of *(177)*. The phosphonium salt *(178)* is the product when tetraphenyldiphosphine, potassium diphenylphosphine or secondary phosphines are used [81-85].

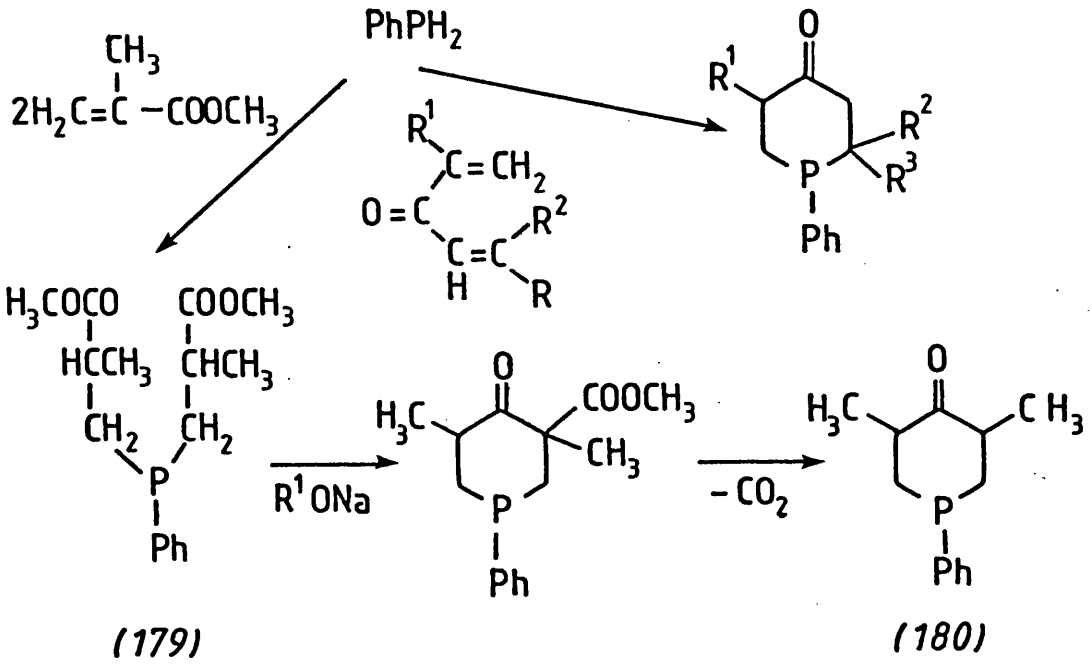


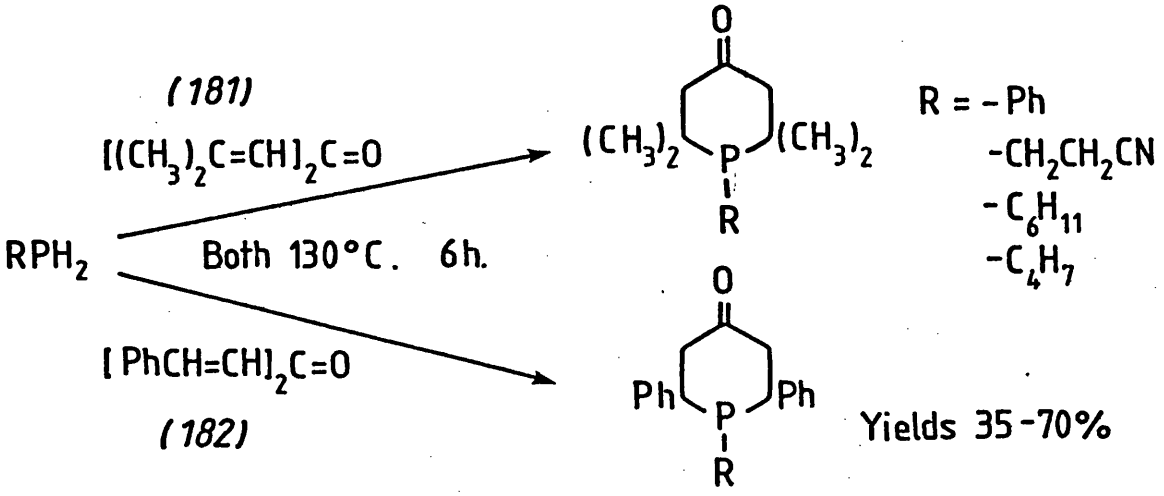
(176) *(177)* *(178)*

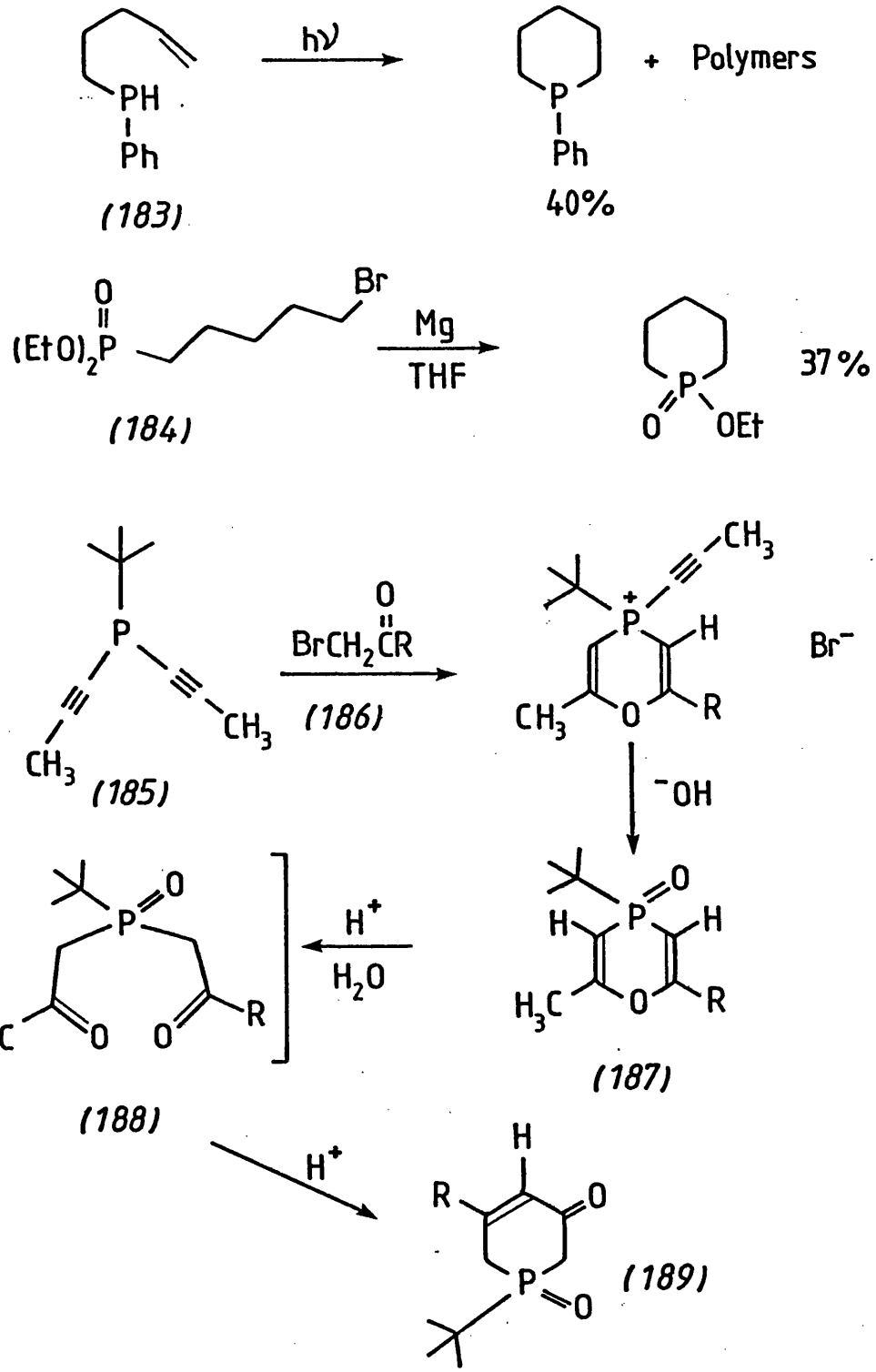
Phenylphosphine ($PhPH_2$) readily adds to the double bond of acrylic and methacrylic esters with the formation of the tertiary phosphines *(179)* which are easily cyclised to form 4-phosphoninanones *(180)* [131].

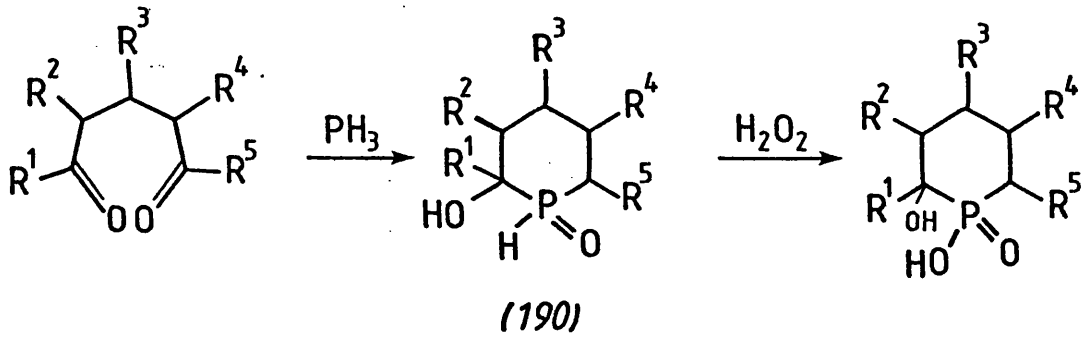
Similarly primary phosphines react with phorone *(181)* and dibenzal-acetone *(182)* in a two-step reaction also to give 4-phosphorinanones in good yields [132]. Other cyclisation reactions include the photo-lysis of secondary alkenyl phosphines *(183)* in about 40% yields [134] and a Grignard cyclisation reaction of diethyl 5-bromopentylphosphonate *(184)* [133].

Markl [135] reported the cyclisation of bis-propinyl-t-butylphosphine *(185)* with the bromoketone *(186)* to yield *(187)*. With aqueous alcohol/

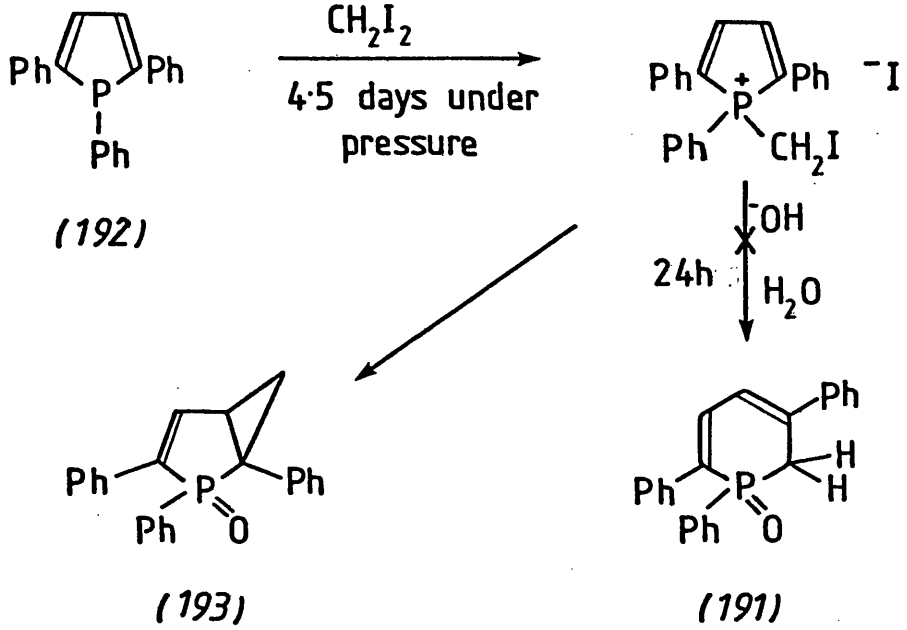

PhPH2
2H2C=C(CH3)-COOCH3
H3COCO COOCH3
HCCH3 CHCH3
CH2 CH2
P
Ph
R1ONa
H3C COOCH3
CH3
-CO2
H3C CH3
(179)
(180)


(181)
[(CH3)2C=CH]2C=O
RPH2
Both 130°C. 6h.
[PhCH=CH]2C=O
(182)
(CH3)2
(CH3)2
R
Ph
Ph
R = -Ph
-CH2CH2CN
-C6H11
-C4H7
Yields 35-70%


hν
PH
Ph
+ Polymers
P
Ph
40%
(183)
O
(EtO)2P
Br
Mg
THF
P
O
OEt
37%
(184)
P
CH3
CH3
(185)
O
BrCH2CR
(186)
CH3
P
H
R
CH3
O
Br−
−OH
H+
H2O
P
O
H3C
O
O
R
(188)
H
P
O
H
H3C
O
R
(187)
H+
H
R
O
P
O
(189)



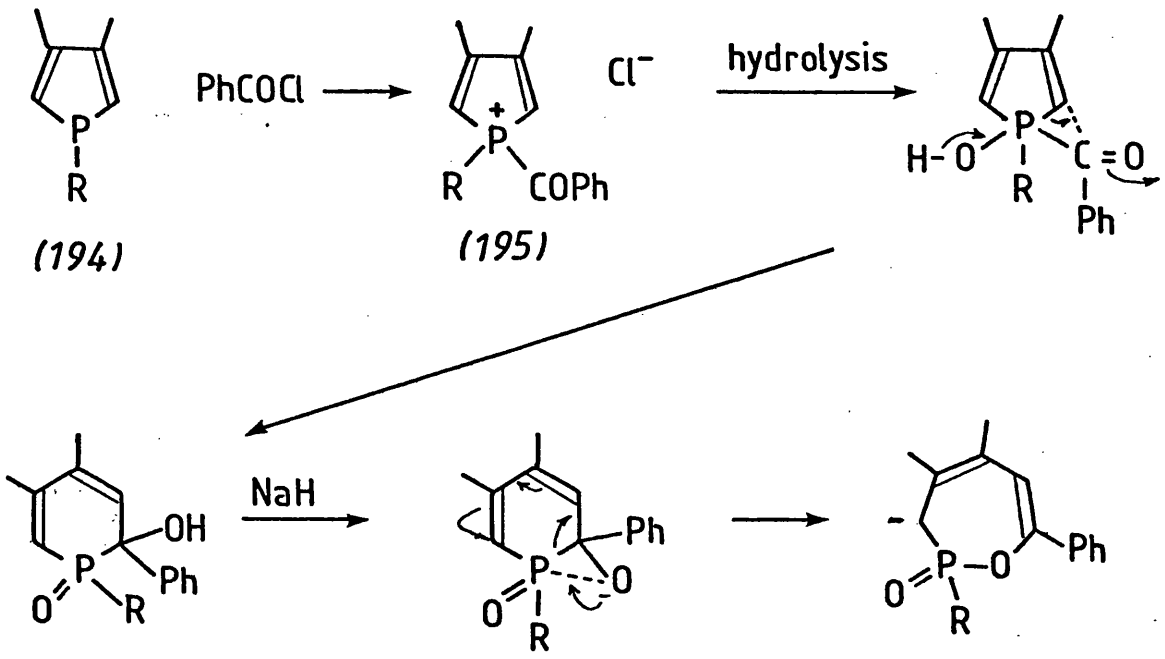
(190)



(192) (193) (191)

conc. hydrochloric acid then the diketone *(188)* is formed which upon further hydrolysis gives the phosphine oxide *(189)* via an acid-catalysed intramolecular aldol condensation. Russian workers have reported that 1,5-diketones reacted with phosphine prepared in situ to give the secondary phosphine oxides *(190)* [136]. These can be oxidised to the phosphinic acids using hydrogen peroxide.

The ring expansion of phosphonium salts upon hydrolysis gave a number



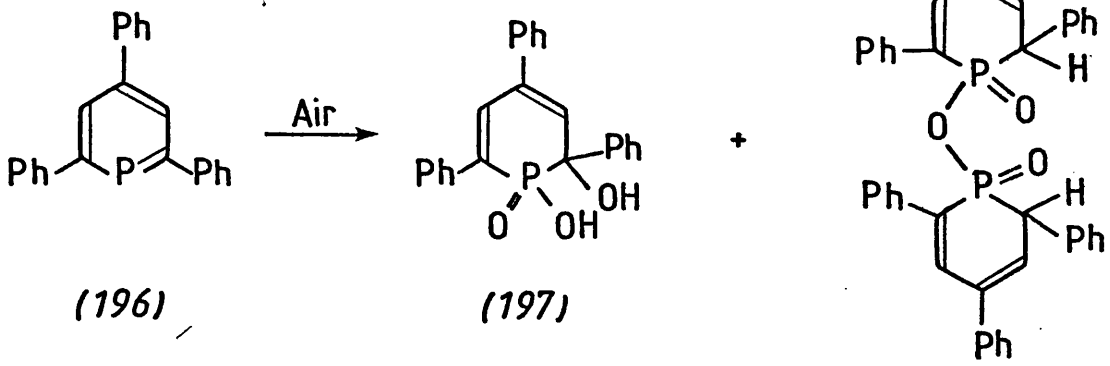
of useful preparations. When Hughes [137] attempted to prepare phosphacyclohexa-2,4-diene *(191)* from 1,2,5-triphenylphosphole *(192)* in this way, instead of *(191)* he obtained *(193)* in 74% yield.

Mathey later showed [138] that such a product *(191)* was an intermediate in the reaction of benzoyl chloride with various phospholes *(194)* after hydrolysis of the phospholium salts *(195)* formed.

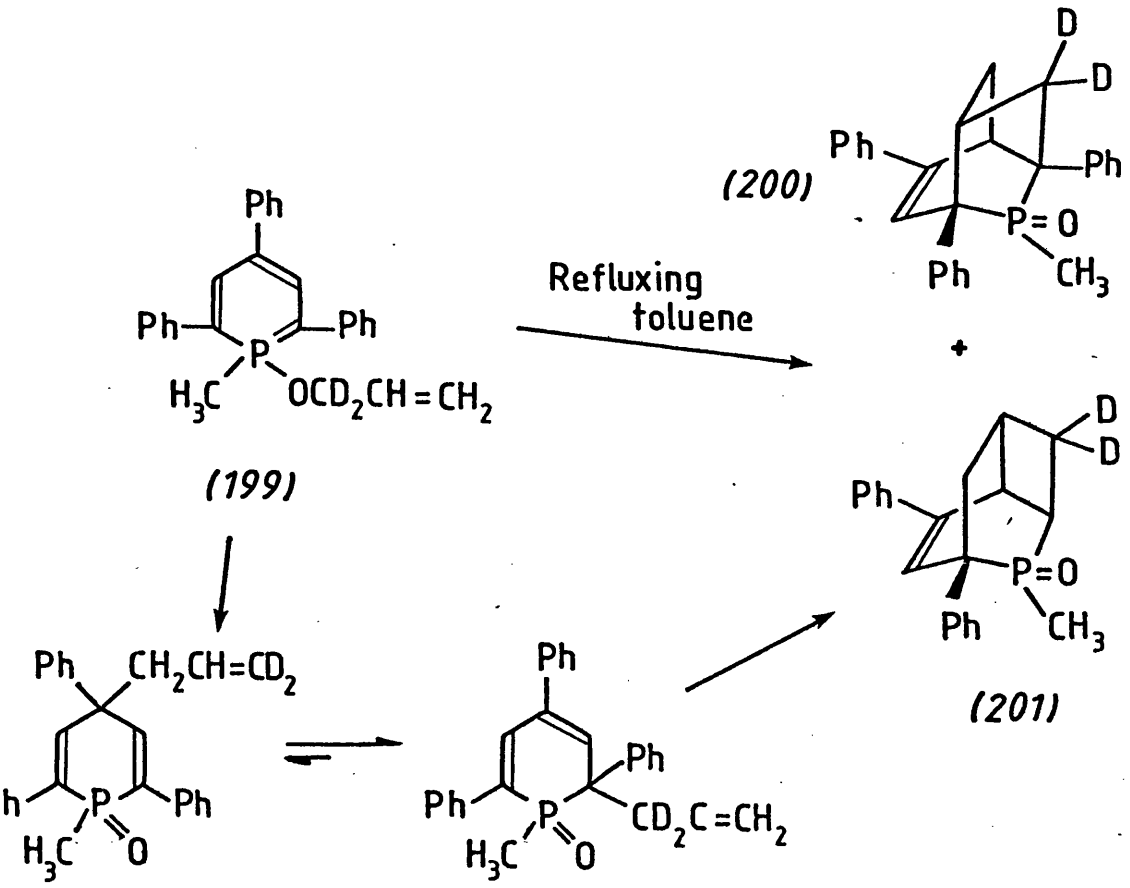
Finally phosphorins which are readily available [86] have proven to be of some use in this field. 2,4,6-Triphenylphosphorin *(196)* left in air for ten days has been shown to yield the products *(197)* and *(198)* [139].

The phosphorin *(199)* upon refluxing in toluene gave the phosphine oxides *(200)* and *(201)*. The authors [141] argue that these compounds are formed after a sigmatropic shift followed by a Diels-Alder reaction.

The phosphorin *(196)* reacted with alkyl lithium or Grignard reagents to form the anions *(202)* and *(203)*, which with alkyl halides gave

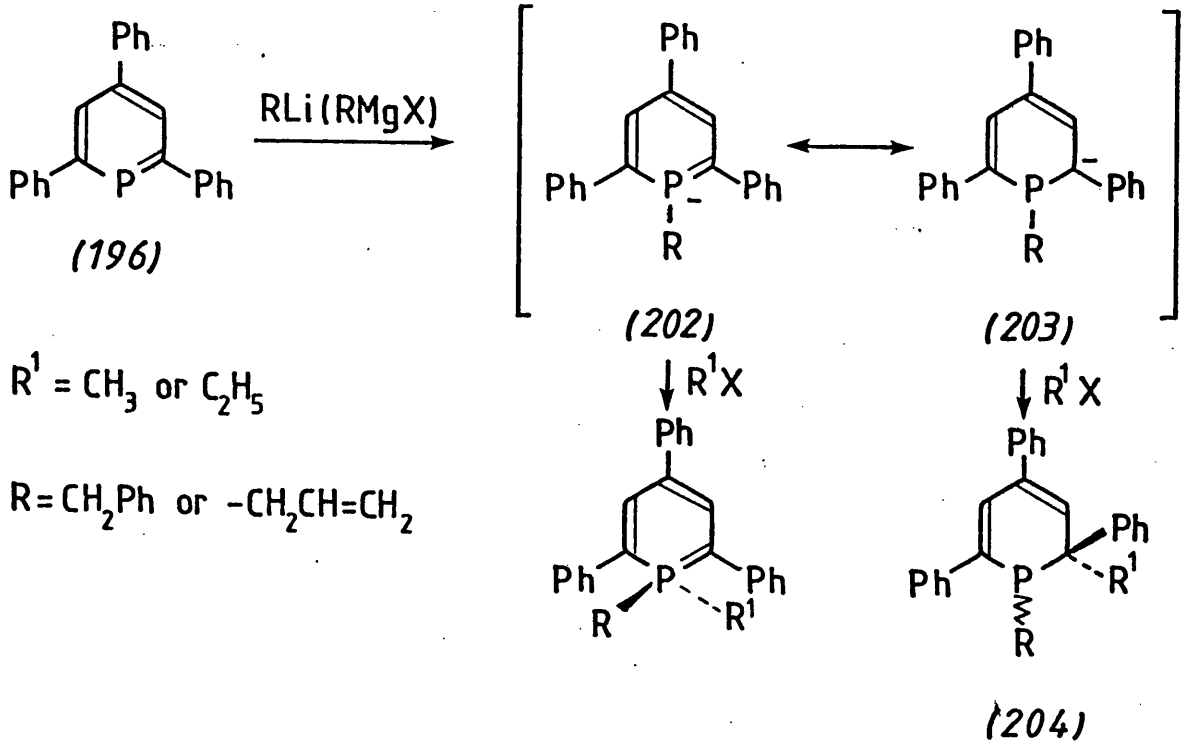


(196) (197) (198)



(199) (200) (201)

either 1,1-dialkyl-2,4,6-triphenylphosphorin or the diene *(204)* [140].

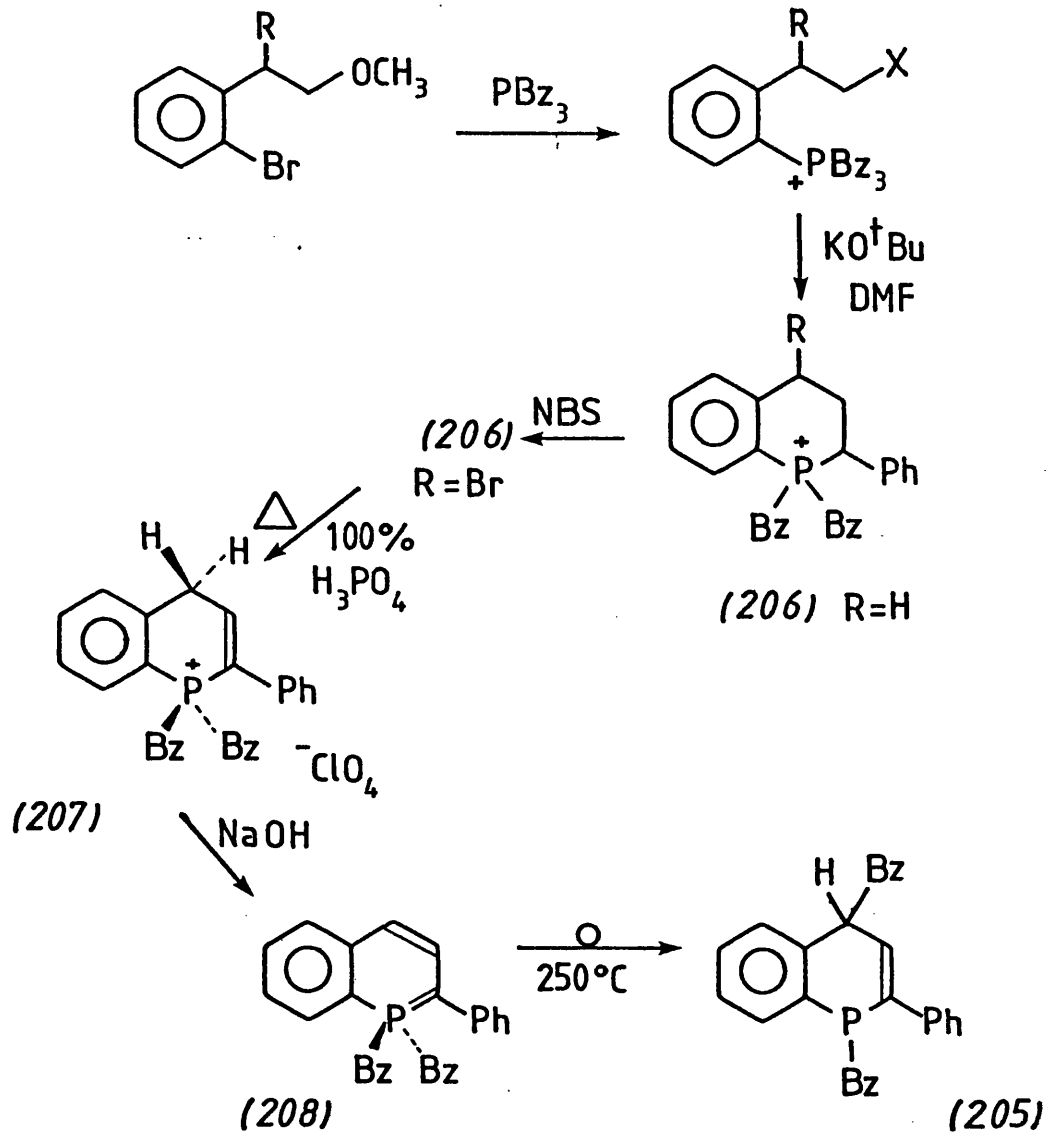


Phosphinoline and Isophosphinolines

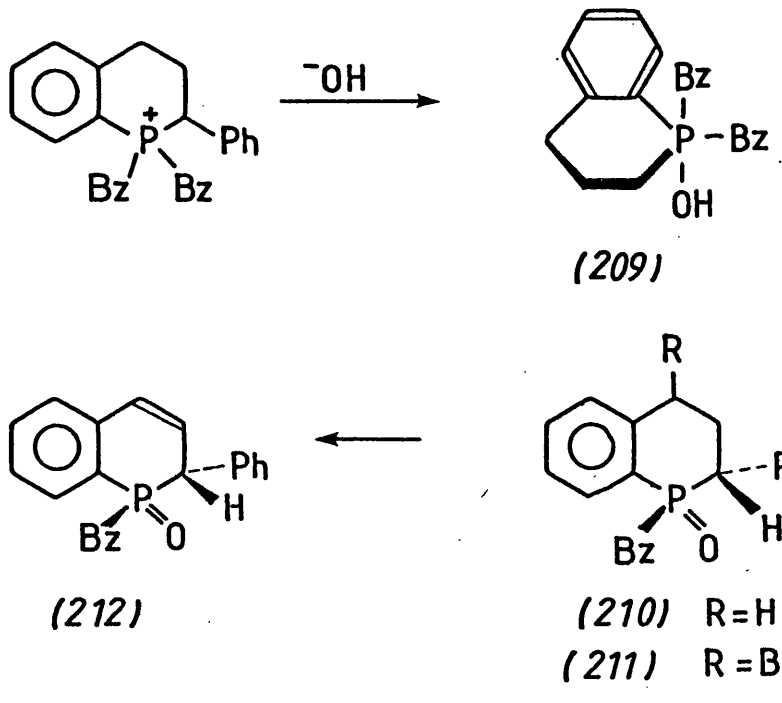
Intramolecular quaternization already mentioned as a route to phosphorinanes can also be used to prepare phosphinolines [87,88,89,90 and 91]. The bromide *(206)* R = Br does not form the 1,2-dihydrophosphinoline upon dehydrobromination but the double bond isomerizes to bring it into conjugation with both the phosphorus atom and the aromatic ring giving *(205)*. Scheme 8.

The alkaline hydrolysis of the tetrafluoroborate salt of *(206)* goes via the pentacoordinate intermediate *(209)*.

In order to facilitate an apical addition and departure the tetrahydrophosphinoline ring has to adopt a diequatorial attachment to phosphorus, the degradation then proceeds smoothly in quantitative

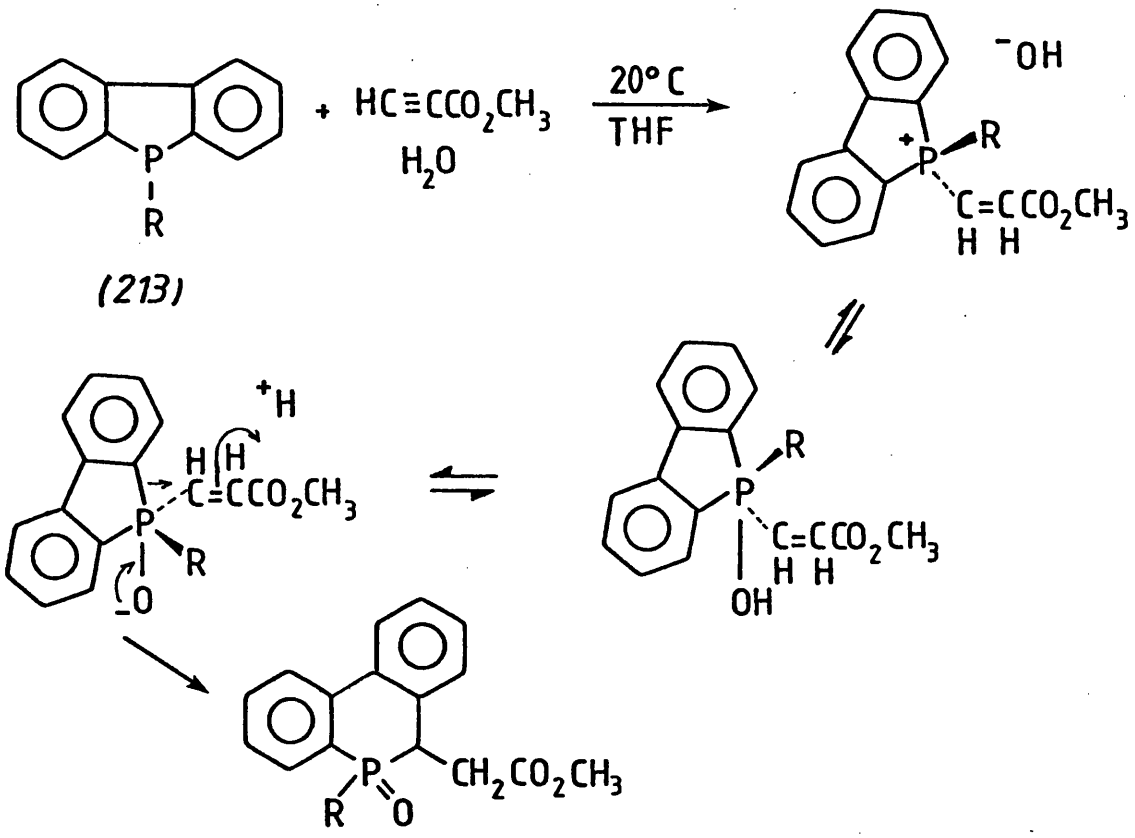

R
OCH3
Br
PBz3
X
PBz3
KO^tBu
DMF
Ph
Bz
Bz
(206) R=H
NBS
(206)
R=Br
100%
H3PO4
H
H
Ph
Bz
Bz
ClO4
(207)
NaOH
O
250°C
H
Bz
Ph
Bz
Bz
(208)
(205)

SCHEME 8


OH
Ph
Bz
Bz
Bz
P
Bz
OH
(209)
R
Ph
H
Bz
O
(210) R=H
(211) R=Br
(212)

yield to give the tetrahydrophosphinoline *(211)*. When brominated with N-bromosuccinimide and dehydrobrominated with lithium bromide in DMF at 150°C, 1-benzyl-2-phenyl-1,2-dihydrophosphinoline 1-oxide *(212)* was obtained in 21% yield from *(210)* [87].

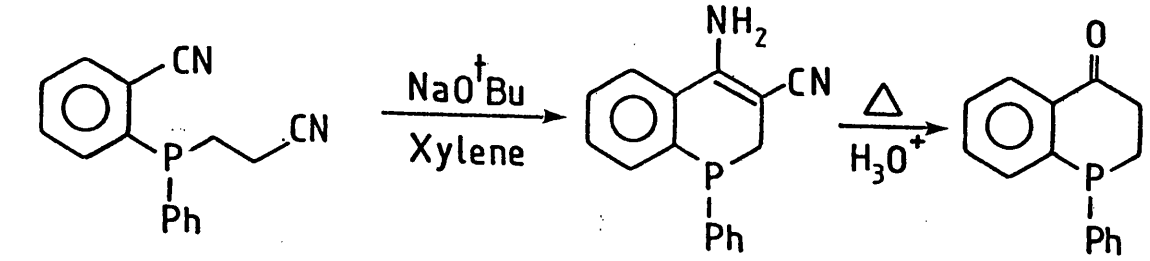
5,6-Dihydrobenzophosphorin 1-oxides have been prepared by Tebby [92] starting from the phosphine *(213)*, methyl propiolate and water.



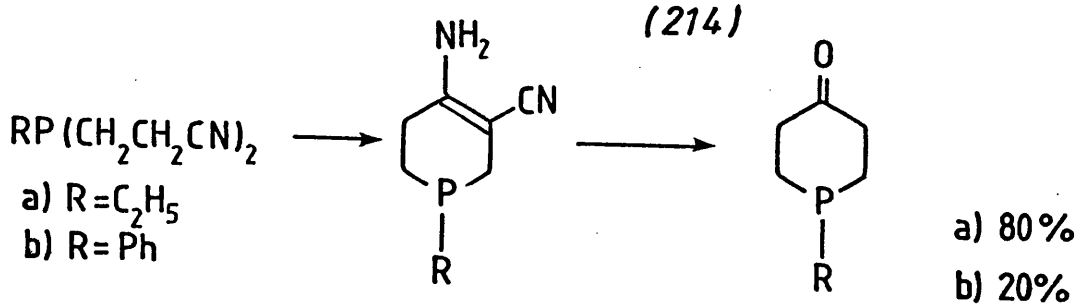
Phosphorinanes [93] and dihydrophosphinolines [94] have both been prepared by the cyclisation of dicyano-compounds with sodium t-butoxide.

The 4-amino-3-cyano-1,2-dihydro-1-phenylphosphinoline *(214)* can be converted into the 4-phosphorinanone in 40% yield [94]. The most general and useful preparation of tetrahydrophosphinolines involves the cyclisation of various acyclic phosphine oxides [95]. Diethyl benzylphosphonite *(218)* a) can be cyclised in this way. The ketophosphinic acid formed can be reduced with sodium borohydride to the 1,2-

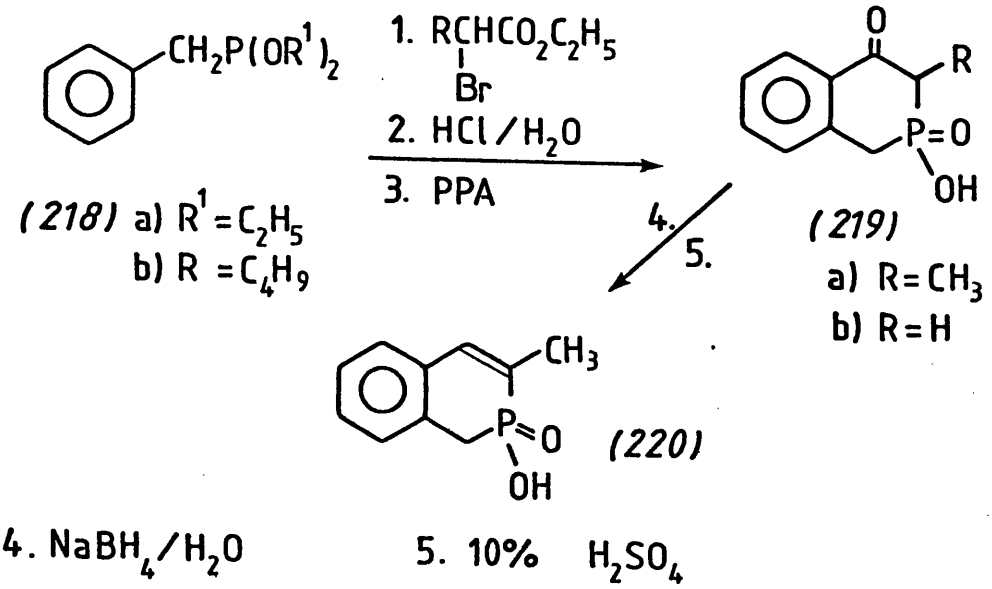
dihydroisophosphinoline oxide *(220)*.



(214)



(215) *(216)* *(217)*

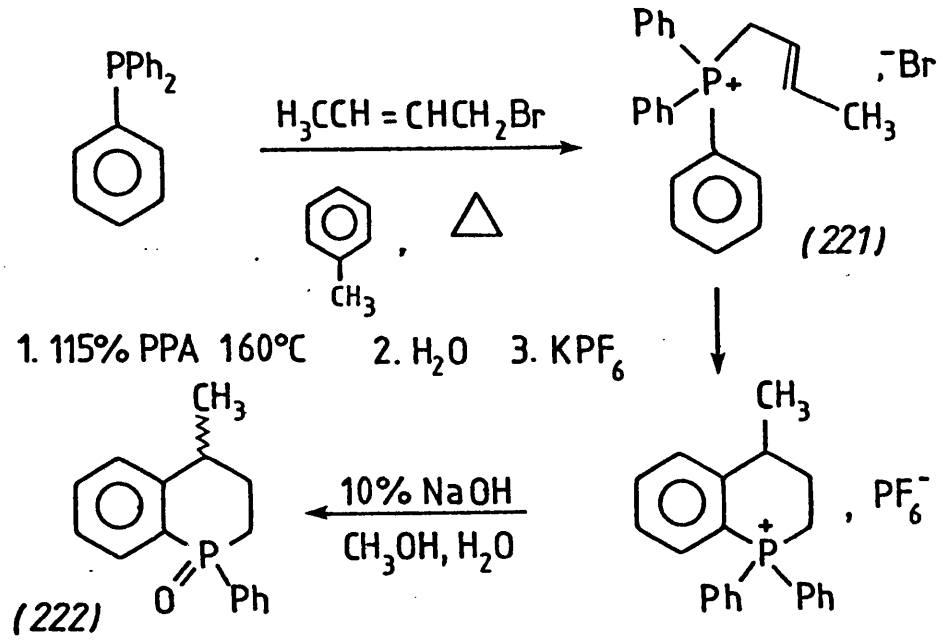


(218) a) $R^1 = C_2H_5$
b) $R = C_4H_9$

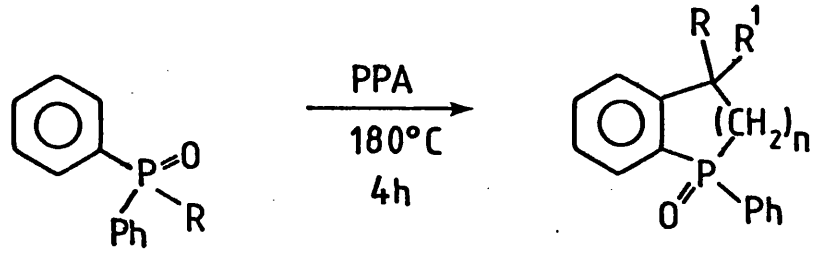
(219)
a) R=CH$_3$
b) R=H

(220)

More recently, work by Berlin [96] has produced tetrahydroisophosphinolinium and tetrahydrophosphinolinium salts from the cyclisation of the phosphonium salts *(221)* containing a β-alkenyl substituent.



Hydrolysis of the resulting phosphonium salts with 10% sodium hydroxide gave 1-phenyl-4-methyl-1,2,3,4-tetrahydrophosphinoline 1-oxide *(222)* as a mixture of isomers. This molecule had also been prepared by Berlin [97] from the appropriate diphenylalkenylphosphine oxide *(223)* along with a range of other tetrahydrophosphinolines and phosphindolines *(224)* a) to d).



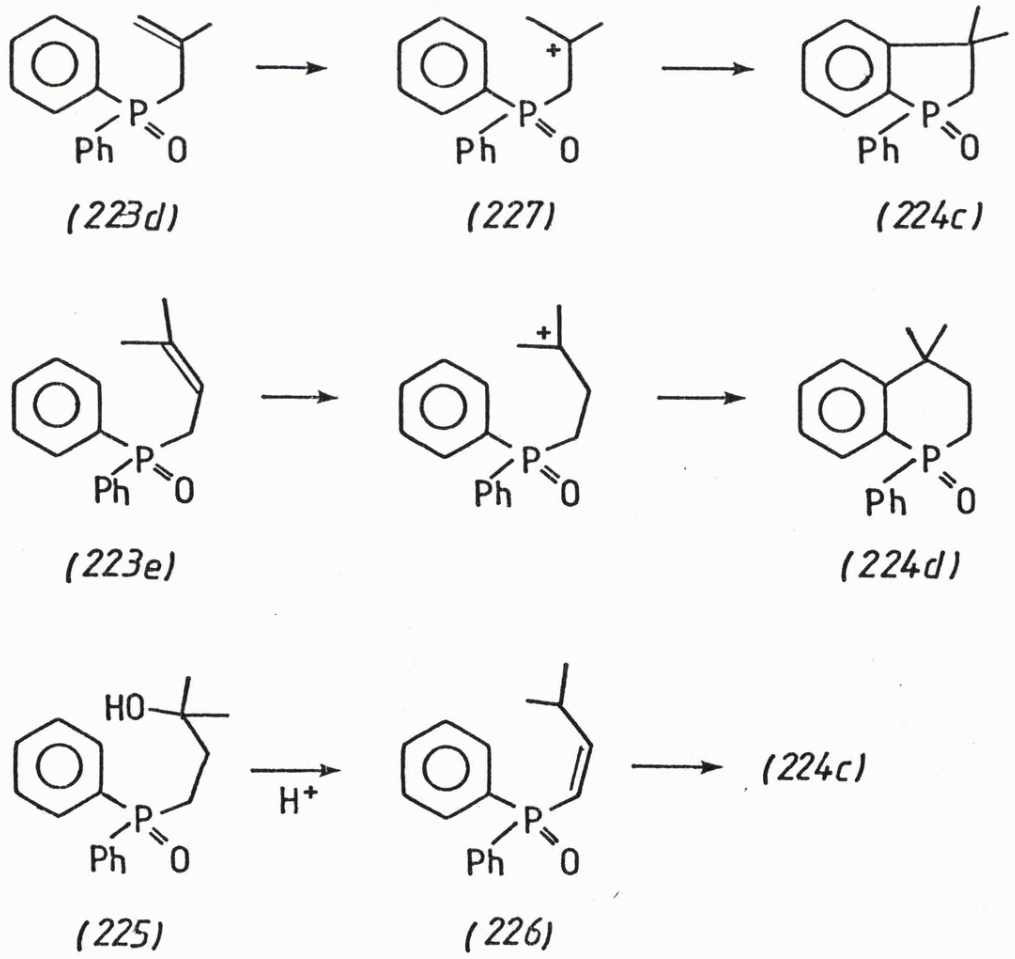
(223)

a. $-CH_2CH=CH_2$
b. $-CH_2CH=CHCH_3$
c. $-CH_2CH_2CH=CH_2$
d. $-CH_2C(CH_3)=CH_2$
f. $-CH(CH_3)CH=CH_2$
g. $-CH(C_6H_5)CH=CH_2$
e. $-CH_2CH=C(CH_3)_2$

(224)	R	R^1	n
a.	H	CH_3	1
b.	H	CH_3	2
c.	CH_3	CH_3	1
d.	CH_3	CH_3	2
f.	polymers		
g.			

One of the reasons why the preparation of these types of molecules is difficult using this route is that a phosphinoyl substituent deactivates the benzene ring towards electrophilic attack [98]. To make the reaction possible the conditions must be very favourable, that is, an intramolecular reaction with a long lived cation. Thus compound *(223)* c) in PPA at 170°C for four hours gave *(224)* c) while, under the same reaction conditions *(223)* e) gave *(224)* d). In both cases the ring size was determined by the most stable carbonium ion that could be formed.

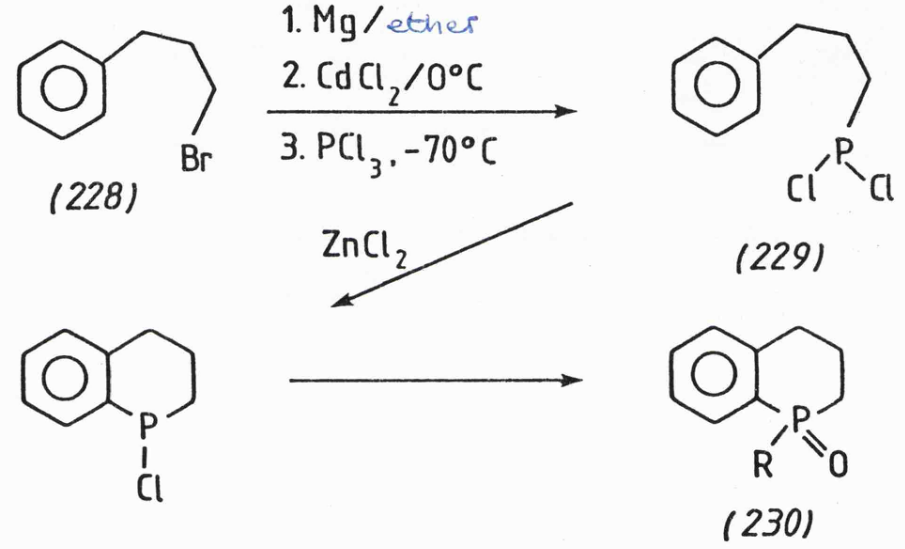
When the β-hydroxyethylphosphine oxide *(225)* was treated with acid under mild conditions, the product isolated was *(226)*. This product was also obtained from *(223)* e) under the same conditions.



When, however, the reaction was made more forcing then both *(223)* e) and *(225)* gave the phosphindoline in high yield. This was attributed to a mechanism involving the same carbonium ion.

In summary, phosphindoline and phosphinoline ring systems may be prepared easily from β-hydroxyalkyl phosphine oxides or diphenylalkenyl-phosphine oxides, as long as the substituents on the alkyl side chain are capable of stabilizing the appropriate carbonium ion.

Swan has produced a synthesis in which the crucial cyclisation step was achieved using a Friedel-Crafts reaction [99,100].



a) R = -H, b) -OH, c) $-OCH_3$, d) $-OC_2H_5$,
e) -Ph, f) $-C_2H_5$, g) - vinyl.

1-Bromo-3-phenylpropane was converted by a modified Grignard reagent (prepared using cadmium chloride) and phosphorus trichloride to 3-phenylpropylphosphonous dichloride *(229)*. This compound was then cyclised with anhydrous zinc chloride to give 1-chloro-1,2,3,4-tetra-hydrophosphinoline which with acid and oxidation with bromine produced the phosphinic acid *(230)* b) in 30% yield (from compound *(228)*). The 1-substituent could be changed via treating the acid chloride with suitable Grignard reagent to give 1-phenyl-, 1-ethyl-, or 1-vinyl-

phosphinoline 1-oxides.

The preparation of 1,2-dihydrophosphinoline 1-oxides

It was decided initially that the best route to 1,2-dihydrophosphinoline 1-oxides would be to use the method of Berlin [97]. Problems arose, however, because although this technique works well on the small scale, 0.5 to 2 g of phosphine oxide being cyclised at a time, when these reactions are scaled up then experimental difficulties arise. Berlin found the optimum ratio of PPA to phosphine oxide to be 50:1, when he attempted to reduce the amount of PPA the yield of tetrahydrophosphinoline was adversely affected.

As large amounts of the tetrahydrophosphinoline oxides were required a new approach was sought. We attempted to reduce the quantities of PPA needed and to replace it in part with a high boiling solvent.

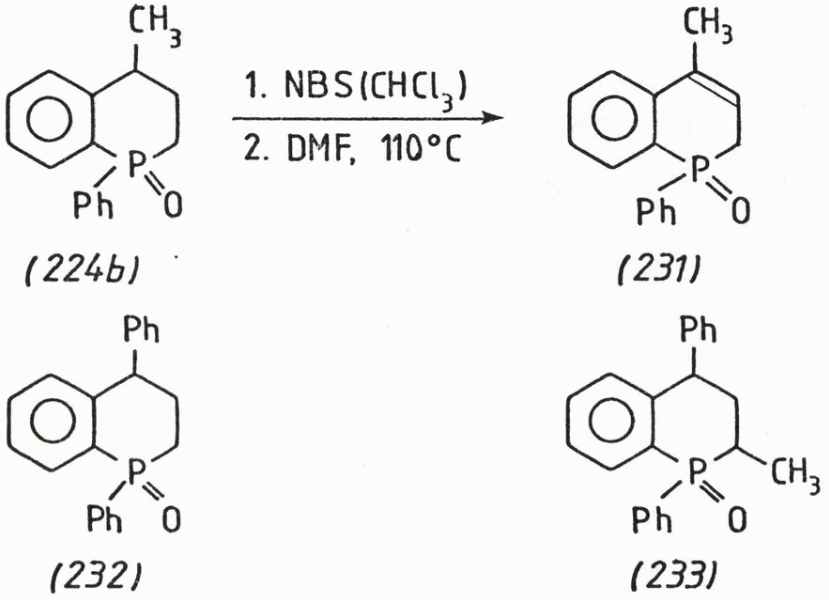
When o-dichlorobenzene was used with a much reduced amount of PPA, good yields were obtained of the tetrahydrophosphinoline oxides.

4-Methyl-1-phenyl-1,2,3,4-tetrahydrophosphinoline 1-oxide *(224)* b) was prepared in excellent yield with a ratio as little as 6:1 (PPA : phosphine oxide).

Diphenylbut-2-enylphosphine oxide (14 g) was added over an hour in o-dichlorobenzene (100 mls) to a mixture of PPA (100 mls) and o-dichlorobenzene (300 mls) at 180°C. The problem with Berlin's technique is that 700 mls of PPA would be required and this would then need very large amounts of water, to quench the reaction, and chloroform to extract the product. Reducing the PPA : phosphine oxide ratio reduces the volume of water and chloroform needed and make large scale conversions of phosphine oxide to tetrahydrophosphinoline possible. This compound was then converted by bromination and dehydrobromination

to 4-methyl-1-phenyl-1,2-dihydrophosphinoline 1-oxide *(231)*.

Attempts to brominate and dehydrobrominate 1,4-diphenyl-1,2,3,4-tetrahydrophosphinoline 1-oxide *(232)* and 2-methyl-1,4-diphenyl-1,2,3,4-tetrahydrophosphinoline 1-oxide *(233)* both failed. These compounds had been prepared by the Warren method [103] of cyclisation, from 1,3,3-triphenylphosphinoylpropan-1-ol and 1,2,2-triphenylphosphinoylbutan-1-ol respectively.



Bromination conditions included the use of N-bromosuccinimide in carbon tetrachloride and irradiation with a spot lamp, the use of bromine in carbon tetrachloride, and also attempts were made with these reagents and the radical initiators benzoyl peroxide and azoisobutyronitrile (AIBN). The use of triphenylmethyl (trityl) fluoroborate was tried, to convert *(232)* into its 1,2-dihydrophosphinoline 1-oxide, but again to no effect.

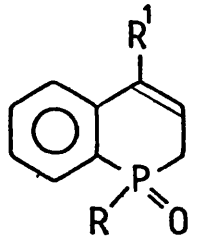
(232) was dissolved in acetonitrile and trityl fluoroborate was added as an acetonitrile solution. The reaction mixture was refluxed for two hours then poured into water and the organic portion extracted

with dichloromethane, only *(232)* was recovered as identified by its ^{31}P and ^{1}H n.m.r. spectra.

These negative results must be explained by a number of factors. One reason why the bromination reactions were not successful might be steric effects, the bulky bromine atom not being able to attack the 4-hydrogen atom because of the three massive phenyl groups blocking its entry. This seems reasonable but does not account for the fact that any radical formed at the 4-position would be stabilised by conjugation and this should help the loss of the hydrogen atom. Another factor which clouds the issue is that *(232)* has two diastereo-isomers while *(233)* has eight isomers. The ^{1}H n.m.r. spectra of these compounds are reduced to very broad singlets. Removal of the 4-hydrogen atom from the spectrum is very difficult to follow. A similar situation also arises with the ^{31}P n.m.r. spectra. Thus although 4-phenyltetrahydrophosphinoline 1-oxides were relatively simple to prepare they could not be converted into their dihydro- equivalents.

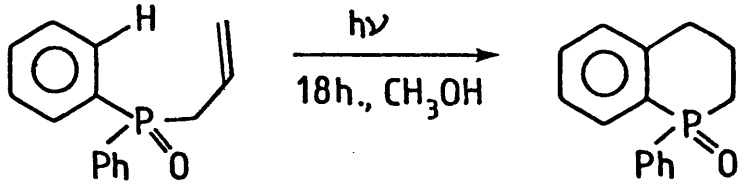
Swan's method was used to prepare 1-methyl- and 1-phenyl-1,2,3,4-tetrahydrophosphinoline 1-oxides (*(230)* R = CH_3 and R = Ph). Both were converted by bromination and dehydrobromination into the appropriate 1,2-dihydrophosphinoline oxides *(234)*. With the exception of 1-phenyl-1,2-dihydrophosphinoline 1-oxide *(234c)*, which was a white crystalline solid, these compounds were all hydroscopic oils.

The preparation of 1-phenyl-1,2,3,4-tetrahydrophosphinoline 1-oxide *(230c)* was attempted photolytically. Diphenylallylphosphine oxide *(235)* was irradiated (λ = 254 nm) in methanol for up to eighteen hours without change.



(234)

	R	R^1
a)	CH_3	H
b)	Ph	CH_3
c)	Ph	H
d)	OCH_3	H

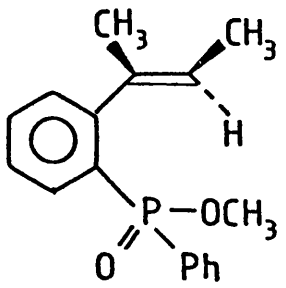


(235) (230e)

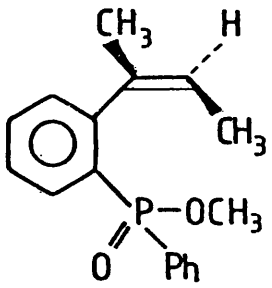
The photolysis reactions of 1-substituted-1,2-dihydrophosphinoline 1-oxides

When 4-methyl-1-phenyl-1,2-dihydrophosphinoline 1-oxide *(234b)* was dissolved in methanol (dry, distilled and degassed) and left for a week in the dark at room temperature, it was recovered quantitatively. Similar dark reactions of the other dihydrophosphinoline oxides also yielded unchanged material. When photolysed with ultra-violet light ($\lambda = 254$ nm) in methanol *(234b)* reacted to form a number of products. These were identified by ^1H, ^{31}P n.m.r. and mass spectrometry to be isomers of methyl phenyl-2-(butenyl)phenylphosphinate *(236)*, *(237)* and *(238)*. The individual assignments of the position of the double bond in these isomers came from the ^1H n.m.r. spectrum.

A two hour photolysis reaction produced *(237)*, (in 55% yield), *(236)* and *(238)* (25% yield) and unchanged starting material *(234b)* (20% yield). These yields varied with solution concentration and irradiation times. Two minor products were also identified, in the g.l.c./mass



(236)



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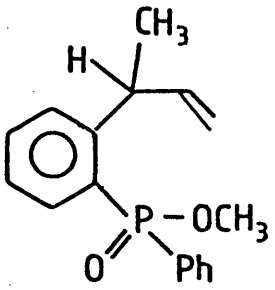


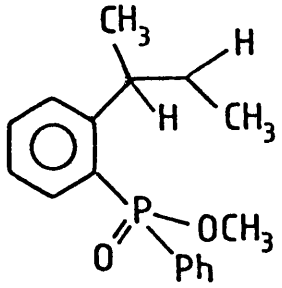
(238)

spectrum of a six hour photolysis, they had parent ions equivalent to adducts of each of these isomers and 4-methyl-1-phenyl-1,2-dihydrophosphinoline 1-oxide.

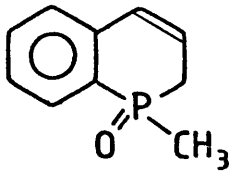
The unchanged starting alkene *(234b)* was separated from the reaction mixture by column chromatography on silica. The individual isomers of methyl-1-phenyl-2-(butenyl)phenylphosphinate however had to be separated by preparative gas chromatography followed by column chromatography. The major isomer was identified as methyl phenyl-2-(trans-2^1-but-2-enyl)phenylphosphinate *(237)*, which was obtained in 60% yield after a six hour irradiation and was a very hydroscopic clear oil.

The separation of the isomeric products proved to be relatively difficult and could only be achieved in poor yield. An attempt was made to alleviate this problem, by converting all three isomers in the photolysis mixture into methyl phenyl-(2-butanyl)phenylphosphinate *(239)*, by hydrogenation.

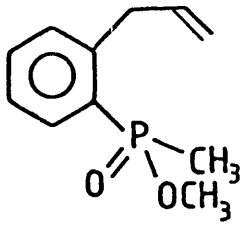
Hydrogenation reactions of the reaction mixture with both 10% palladium upon charcoal and 10% platinum upon charcoal, for up to forty-eight hours, only converted any remaining 4-methyl-1-phenyl-1,2-dihydrophosphinoline 1-oxide *(234b)* into the corresponding tetrahydro-derivative *(224b)*.



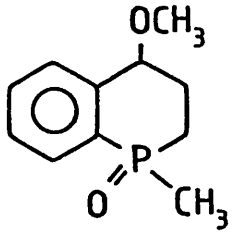
(239)



(234a)



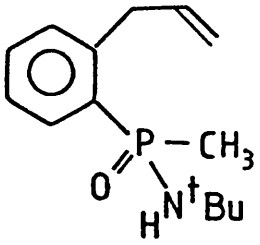
(240)



There were also two minor products present with ^{31}P n.m.r. values of -44 p.p.m., however these could not be separated from the reaction mixture, which still contained all three isomers of *(236)* unchanged, as the major products.

Photolysis of 1-methyl-1,2-dihydrophosphinoline 1-oxide *(234a)* in methanol for one-and-a-half hours gave predominately one product, in 75% yield. This compound was separated from the three minor products by column chromatography, followed by preparative gas chromatography. It was identified as methyl methyl-2(prop-2^1-enyl)phenylphosphinate *(240)*. This product was another hydroscopic oil that failed to give satisfactory analytical results despite the precautions taken. The analysis of this compound, however, was obtained by Gray [130] using

high resolution mass spectroscopy. He also showed that 1-methyl-1,2-dihydrophosphinoline 1-oxide when photolysed in t-butylamine gave N-t-butyl-methyl-2-(prop-2[1]-enyl)phenylphosphorus amide *(241)*.



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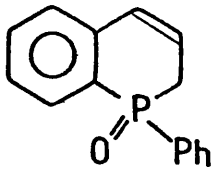
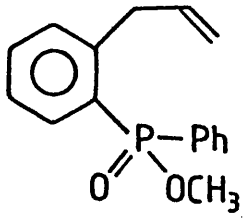


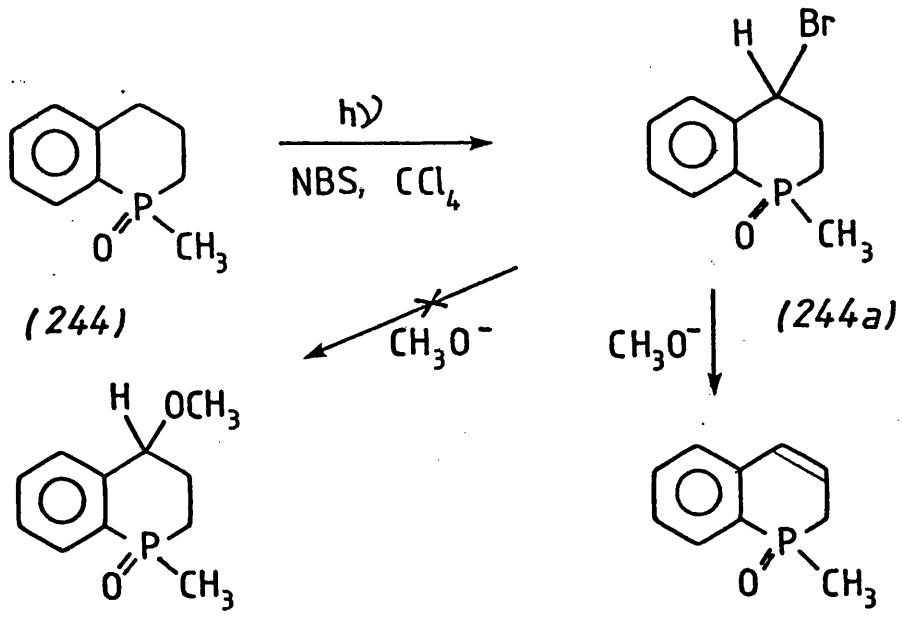
(234c)



(242)

A minor product in the reaction mixture had a similar ^{31}P n.m.r. value to the starting material, and it was thought possible that it was simply the adduct of methanol across the double bond of the 1,2-dihydrophosphinoline 1-oxide molecule. Attempts to prepare 4-methoxy-1-methyl-1,2-dihydrophosphinoline 1-oxide *(243)* by an independent route failed to give the required product. The first attempt was with 1-methyl-1,2,3,4-tetrahydrophosphinoline 1-oxide *(244)* converting it to the 4-bromo compound *(244a)* and treating this with sodium methoxide in methanol, only *(234a)* was obtained. Presumably the sodium methoxide used was acting preferably as a base rather than as a nucleophile. Attempts at converting 1-methyl-1,2-dihydrophosphinoline 1-oxide to *(243)* with mercuric acetate, a reagent commonly used for similar reactions [144,145], followed by sodium borohydride to break up the mercury complex, gave only unreacted starting material, with a 55% recovery.

1-Phenyl-1,2-dihydrophosphinoline 1-oxide *(234c)* when photolysed for

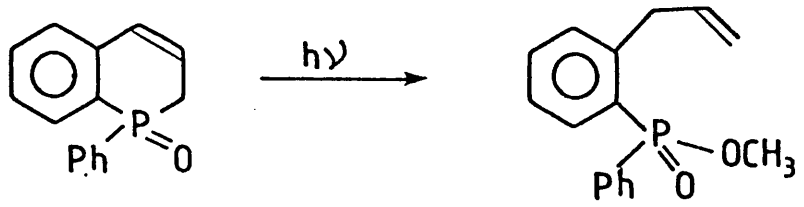


(244) (244a) (243)

three hours in methanol gave predominately one product, in 66% yield as shown by its ^{31}P n.m.r. spectrum. It was not possible to separate this totally from the other two isomers which were easily identified in the ^{1}H n.m.r. spectrum of *(245)* as they contain an extra methyl group (1.3-1.9 δ, m) instead of a methylene group and two olefin hydrogen atoms instead of the three, one at 5.6-6.4 δ, m, and two at 4.8-5.2 δ, m. However, it was identified by ^{31}P and ^{1}H n.m.r., its mass spectrum and IR as methyl phenyl-2-(prop-2^{1}-enyl)phenylphosphinate *(245)*, again this oil failed to give a satisfactory elemental analysis, because of its extreme hydroscopic nature.

The photolysis of 1-methoxy-1,2-dihydrophosphinoline 1-oxide *(246)* in methanol for twenty-six hours yielded dimethyl-2-(prop-2^{1}-enyl)-phenylphosphonate *(247)* in 82% yield as a clear oil.

When 4-methyl-1-phenyl-1,2-dihydrophosphinoline 1-oxide was photo-



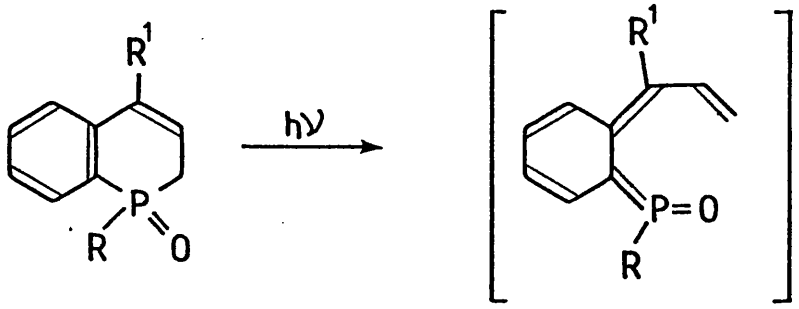
(234c) (245)

lysed in t-butylamine a similar reaction took place as the reaction in methanol. After one-and-a-half hours two products appeared by gas chromatography, after a further one-and-a-half hours all the starting material had been converted into these products. Separation by column chromatography and distillation gave a clear oil which was identified as N-t-butyl phenyl-2-(2^1-but-3-enyl)phenylphosphorus amide *(251)* in 34% yield. The product was identified as the 2^1-but-3-enyl isomer from its 100 MHz ^{1}H n.m.r. spectrum giving a characteristic set of peaks in the olefin region. The two methylene protons appearing at between 4.8 and 5.6 δ as a multiplet and the third olefin proton at between 5.7 and 6.5 δ as a broad multiplet. A similar reaction was also observed when *(234b)* was photolysed in t-butanol.

(246) (247)

All the above results can be rationalised as being reactions involving reactive intermediates of the type *(248)*.

Such intermediates would be the phosphorus analogues of o-quino dimethanes and benzoazahexatrienes mentioned earlier. As such, their



(248)

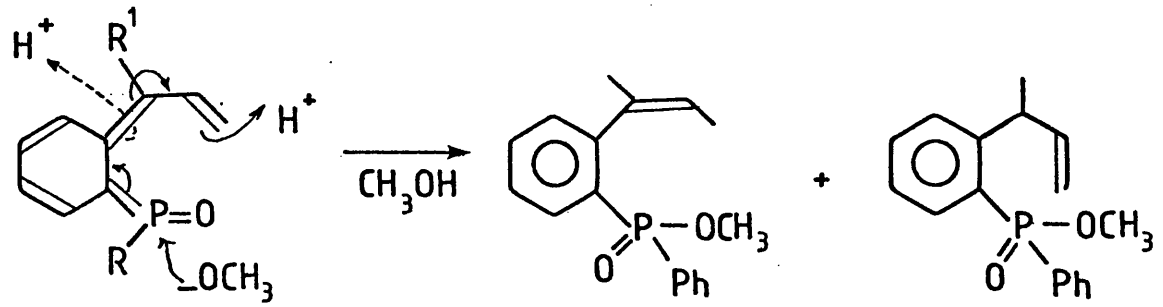
formation must be seen in terms of an electrocyclic ring opening reaction of the starting 1-substituted-1,2-dihydrophosphinoline 1-oxides. All the products obtained were then either [1,4]- or [1,6]-methanol adducts to these intermediates.

When R= methyl and R^1 = Ph, the photolysis in methanol yielded mainly the [1,6]-adduct, *(236)* or *(237)*, thus the methyl group may have sterically hindered the formation of the [1,4]-adduct *(238)*. Alternatively one might initially form *(249)* which isomerises to the more stable *(250)*.

In the t-butylamine case the isomerization was presumably not favoured because of the bulky t-butyl group. With the other alkenes that had no 4-alkyl substituent that isomerization did not take place because the initial prop-2-enyl isomer was the most stable olefin.

Previous work on analogous systems had failed to produce adducts of the reactive intermediate and any species other than an alcohol [75]. The majority of intermediates had undergone intramolecular reactions.

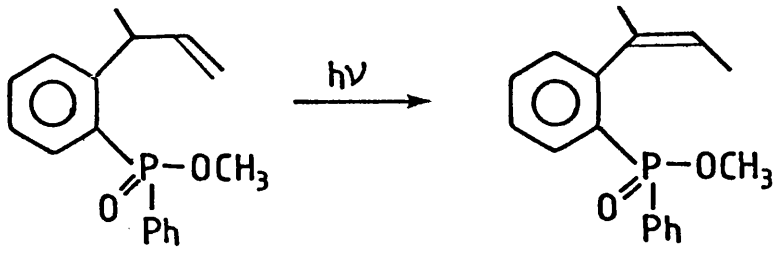
Attempts to trap the species *(248)* using other trapping reagents were made. Photolysis reactions were carried out in acetonitrile, as an inert solvent, and reagents such as tetrachloroethylene and dimethyl acetylenedicarboxylate, both dienophiles. Reaction did occur but it was not possible to isolate any products from these reactions, although ^{31}P n.m.r. spectra showed very complex chemical compositions. It was



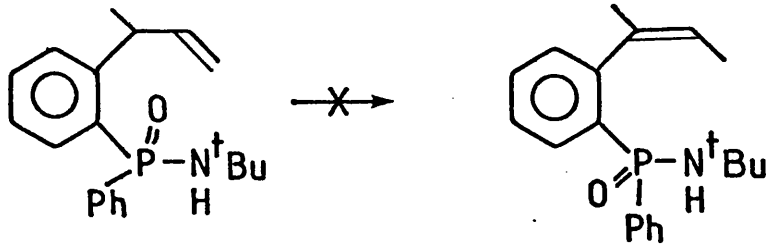
(248) *(236)* & *(237)* *(238)*

(cis) (trans)

[1,4] addition-, [1,6] addition

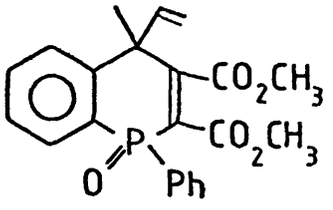


(249) *(250)*



(251) *(252)*

clear that reactions of some kind were taking place, the problem was the retrieval of the products once formed. All the expected adducts, *(253)* to *(256)* inclusive, would have been extremely polar and as shown by thick layer chromatography impossible to isolate from silica and alumina plates. Attempts to distil out the products only produced polymeric material.



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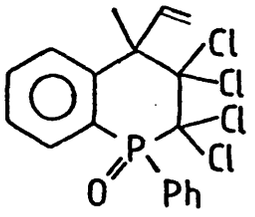

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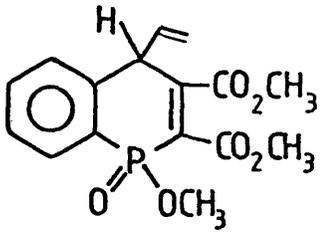

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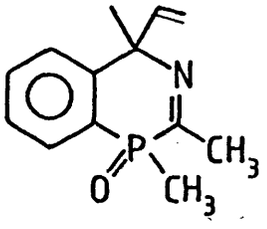


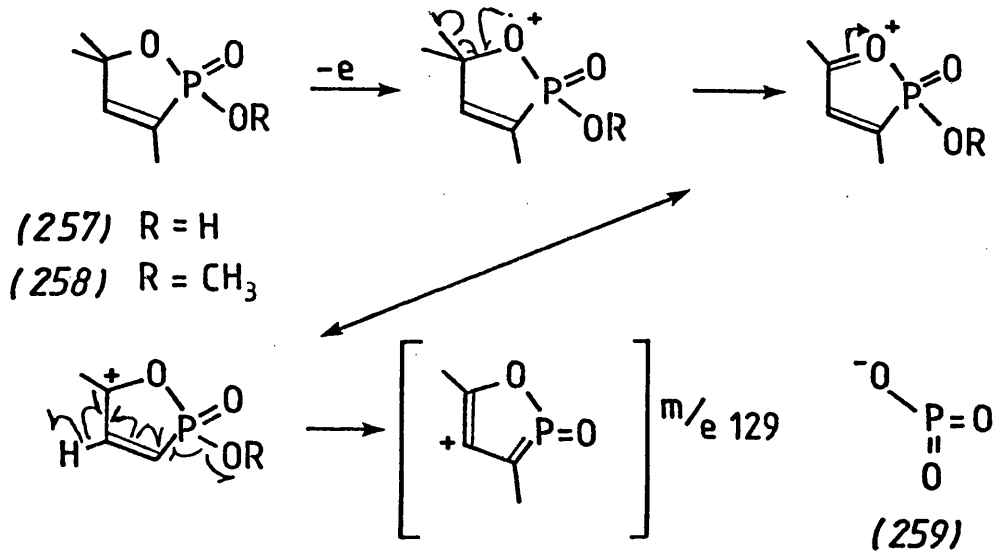
(256)

CHAPTER FOUR

CHAPTER FOUR

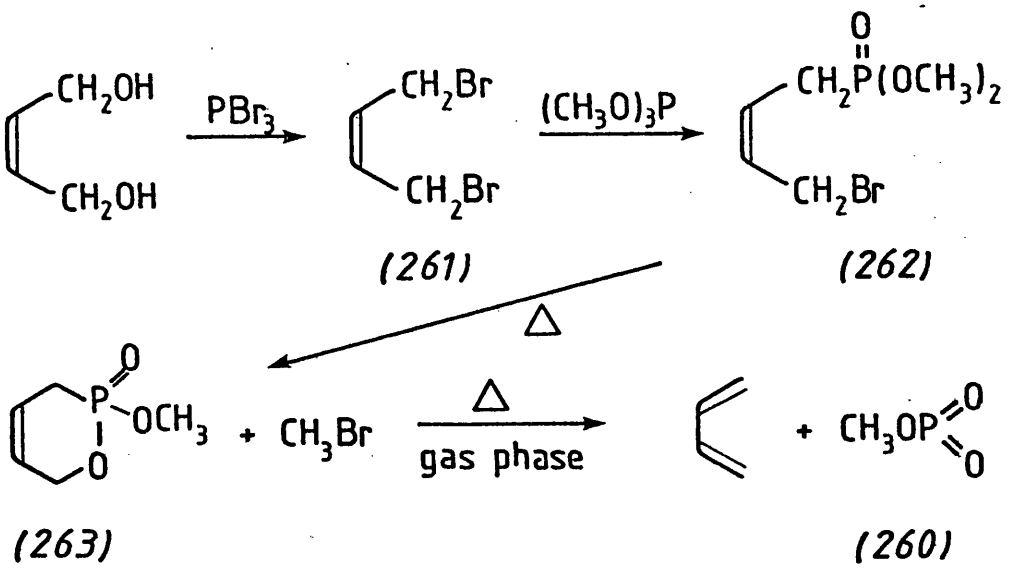
SOME REACTIONS OF OXAPHOSPHOLENE DERIVATIVES

Earlier work [106] has shown evidence of the existence of a 1,2-oxaphosphol-1,3-dienyl species in the mass spectra of compounds *(257)* and *(258)*. Such a fragment has a structure analogous to the monomeric metaphosphate ion *(259)*, it is also a six electron 'aromatic' system and might be expected to gain stability, because of this.



The monomeric metaphosphate ion *(259)* and esters of monomeric metaphosphoric acid have been postulated as intermediates in numerous phosphorylation reactions [107], in the hydrolysis of monoesters of phosphoric acid [108] and in the hydrolysis of various esters of pyrophosphoric acid [109].

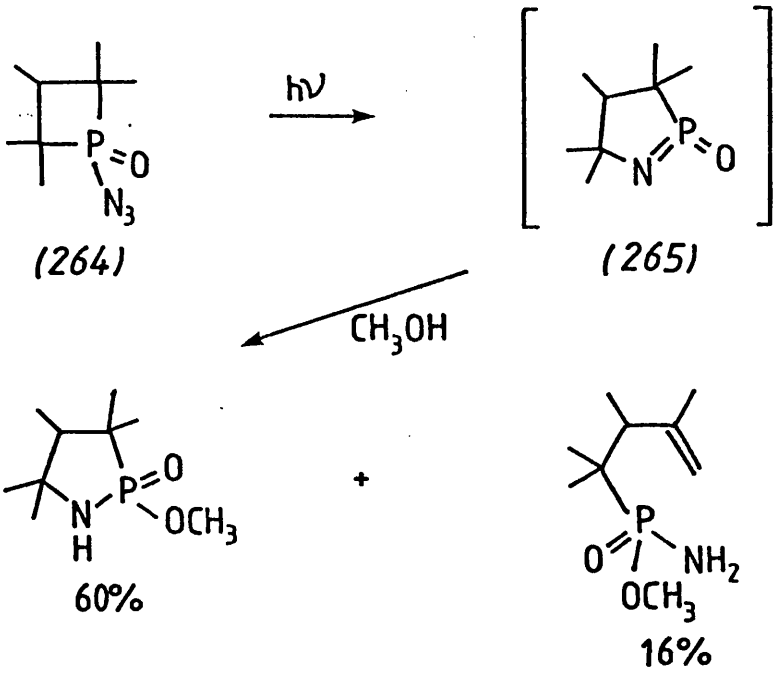
Monomeric methyl metaphosphate [110] was first prepared by Westheimer, and trapped with N-methylaniline, although they later found [111] that *(260)* would attack the aromatic ring of N,N-diethylaniline at low temperatures.



The route used to prepare *(260)* is cis-1,4-dibromobut-2-ene *(261)* reacting smoothly with trimethyl phosphite to yield dimethyl 4-bromo-but-2-enylphosphonate *(262)*, this then cyclised to the required methyl but-2-enylphosphonate *(263)*. Vacuum flash pyrolysis of *(263)* gave methyl polyphosphate in the trap of the apparatus. When N-methyl-aniline was present, then the N-methylanilinium salt of methyl N-methyl-N-phenyl-phosphoramidate was obtained.

Westheimer [112] has postulated the intermediacy of monomeric meta-phosphorimidate *(265)* following similar work by Harger [105] in the photolysis of either cis- or trans-1-azido-2,2,3,4,4-pentamethyl-

phosphetan 1-oxide *(264)* in methanol.

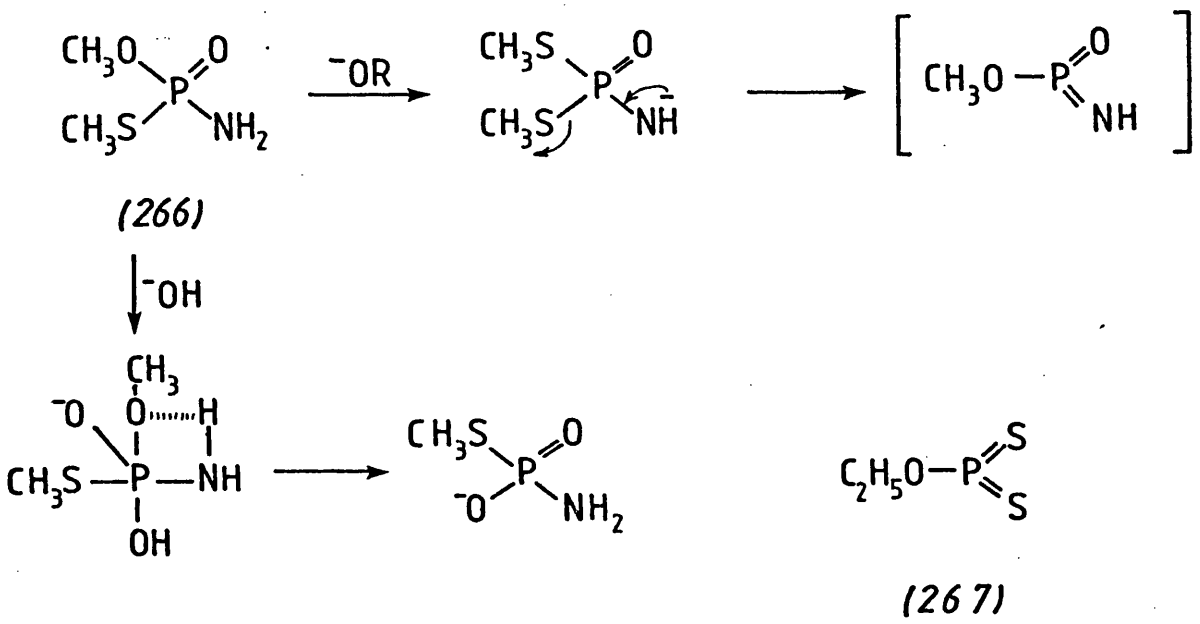


O,S-dimethylphosphoramidothioate *(266)* showed unexpected solvolytic behaviour in base [113], since reaction with hydroxide led mainly to P-O bond cleavage whereas with alkoxides P-S bond cleavage predominated. For the N,N-dimethyl derivative not only was hydroxide attack much slower but, in contrast, gave exclusively P-S bond cleavage. On the basis of this evidence the authors suggested that with strongly basic conditions *(266)* solvolyses via a metaphosphorimidate intermediate resulting from P-S bond breakage.

Under milder basic conditions an SN_2 displacement of methoxide ion assisted by an intramolecular proton transfer was proposed.

Finally, the formation of O,O,S-triethylphosphorodithioate together with triethylthionoformate when triethylorthoformate was treated with P_4S_{10} or diethyl hydrogen dithiophosphate was interpreted in terms of an ethyl dithiometaphosphonate [114] *(267)*.

Perthiophosphinic anhydrides *(268)* react with conjugated dienes to



(266)

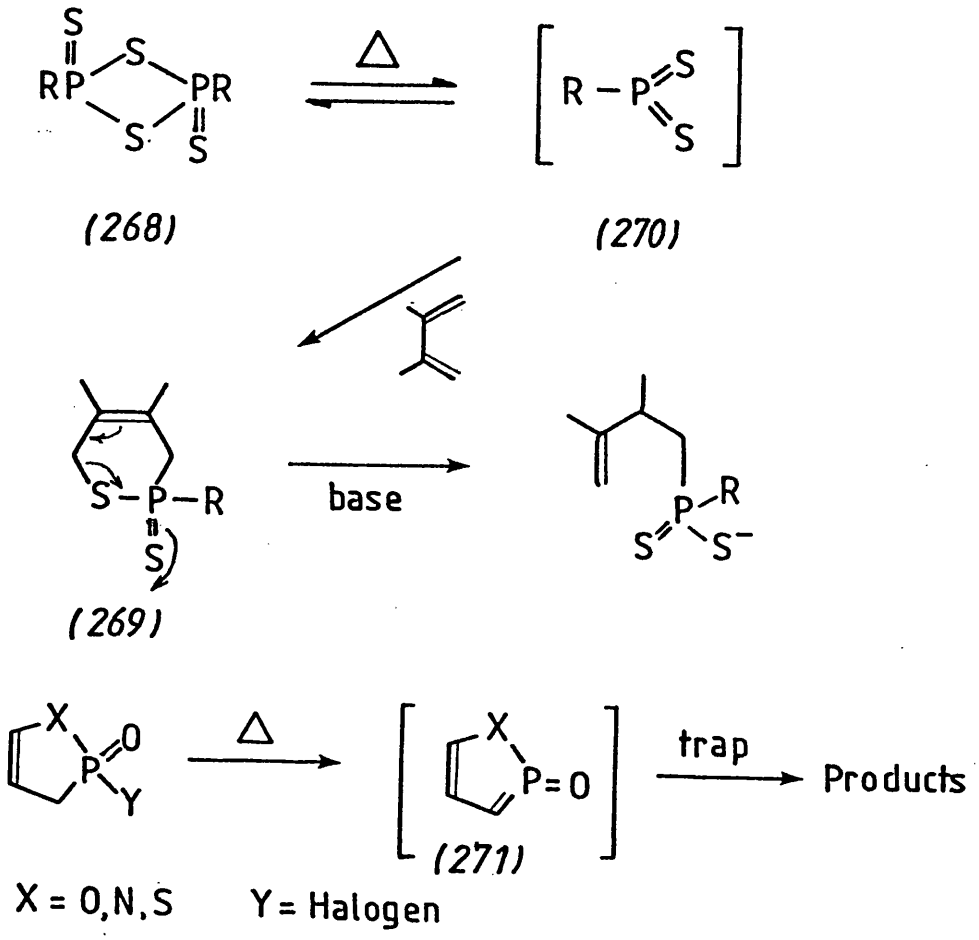
(267)

give the cyclic esters *(269)*, which are cleaved upon treatment with base.

The authors presume the reaction involves the monomer *(270)* in a $2\pi + 4\pi$ reaction with the diene.

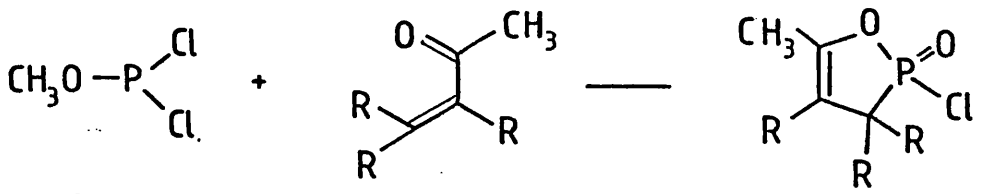
Further reactions of oxaphospholenes have been described by Voncken [121] and by Boutagy [122].

The 1,2-oxaphosphol-1,3-dienyl *(271)* x = o species and its nitrogen and sulphur analogues may be generated in a flash vacuum thermolysis apparatus from the corresponding 1-substituted-phosphol-3-ene. The substituent would have to be a good leaving group such as a halogen. The evidence that such a reaction might be conceivable, comes from the presence of *(271)* x = o in the mass spectra of a number of 1,2-oxaphosphol-3-enes 2-oxides [106].



Preparations of 1,2-oxaphosphol-3-ene 2-oxides

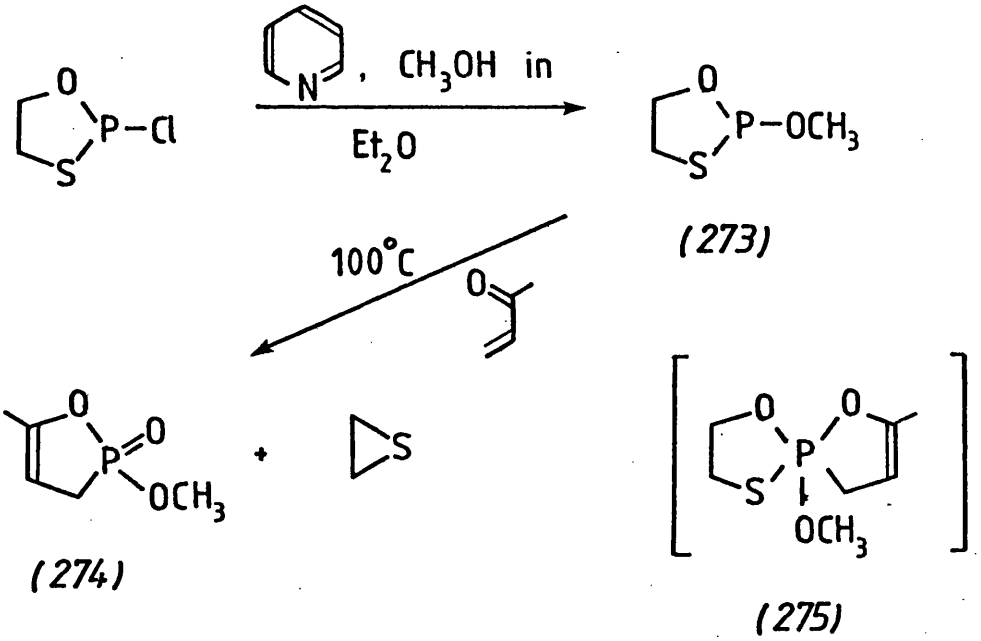
A number of 1,2-oxaphosphol-3-ene 2-oxides can be prepared by the method of Petrov et al. [128]. This method involves mixing equimolar



(272)

amounts of unsaturated ketones or acids with dichloromethoxyphosphine *(272)* at between 5-10°C.

The same workers developed an alternative method of preparation [117], which starts from readily available 2-chloro-1,3,2-oxathiophospholan which was converted with methanol in ether into 2-methoxy-1,3,2-oxathiophospholan *(273)*. Heating *(273)* with methyl vinyl ketone at



(273)

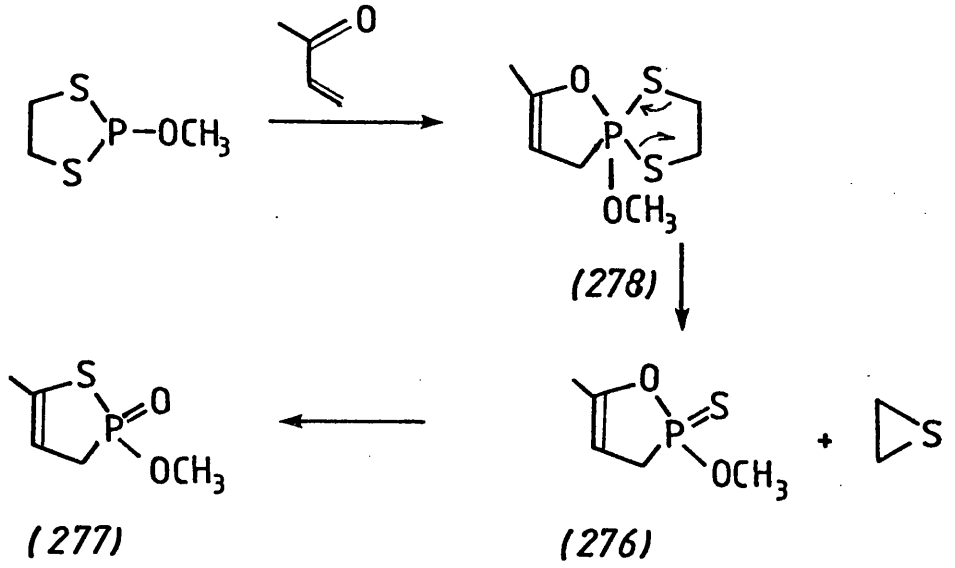
(274)

(275)

between 90-100°C for three hours produces 2-methyl-2-methoxy-1,2-oxaphosphol-3-ene 2-oxide *(274)*. The reaction must proceed via the phosphorane *(275)* which under these conditions decomposes as shown to give the products.

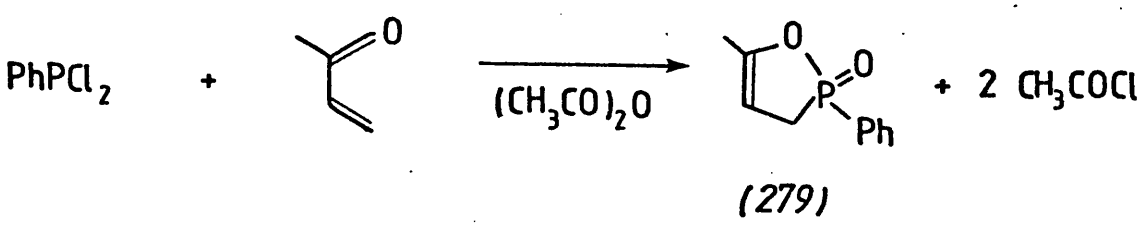
Interestingly the same reaction using 2-methoxy-1,3,2-dithiophospholan

and methyl vinyl ketone did not give the expected product *(276)* but 5-methyl-2-methoxy-1,2-thiophosphol-3-ene 2-oxide *(277)*, presumably going through the intermediates *(278)* and *(276)*. This rearrangement may be explained in the greater stability of the P=O bond relative to the P=S bond.



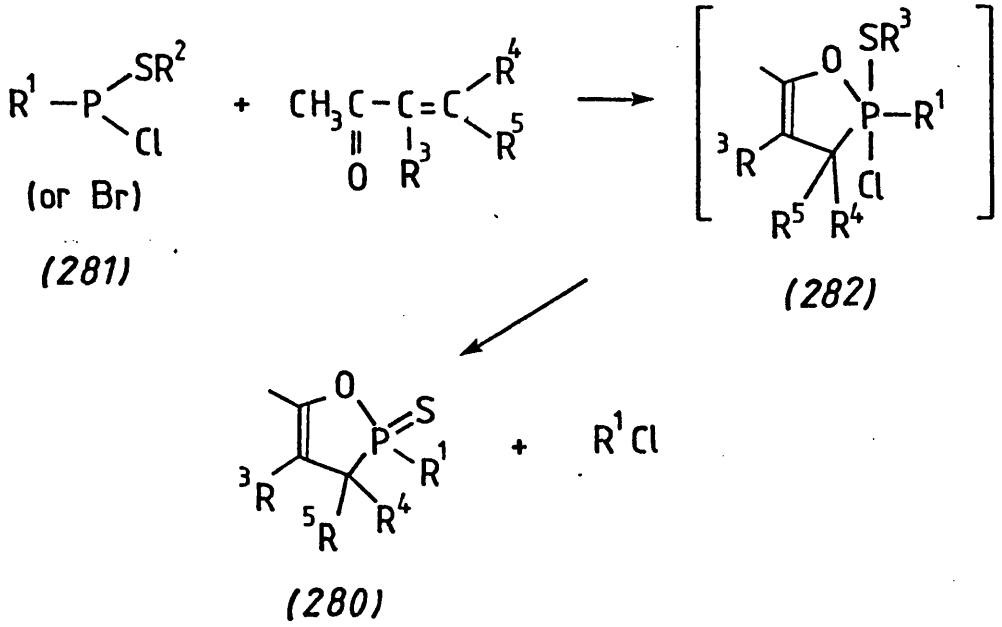
(277) *(276)*

Methyl vinyl ketone will react with dichlorophenylphosphine [115] in the presence of acetic anhydride to give 5-methyl-2-phenyl-1,2-oxaphosphol-3-ene 2-oxide *(279)* and two moles of acetylchloride.



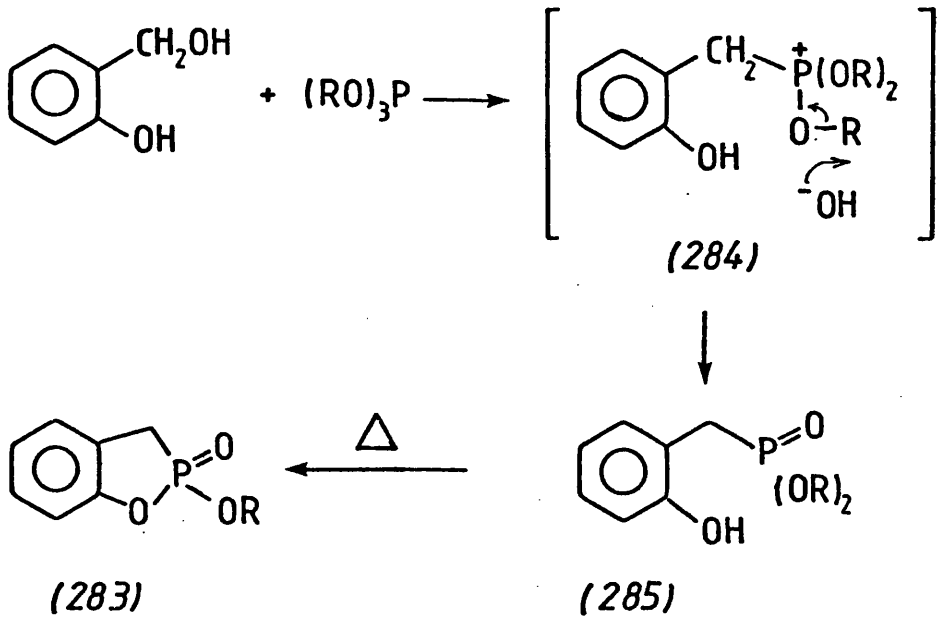
(279)

Work by Akamsin [119] has produced a synthesis of the 2-sulphide *(280)* from the reaction between unsaturated ketones and the compound *(281)*, the initial adduct *(282)* is formed by the 1,4-addition of an α,β-unsaturated compound and *(281)*. Decomposition <u>via</u> the second step of the Arbuzov rearrangement with the cleavage of alkyl halide forms *(280)*.



(281) (282) (280)

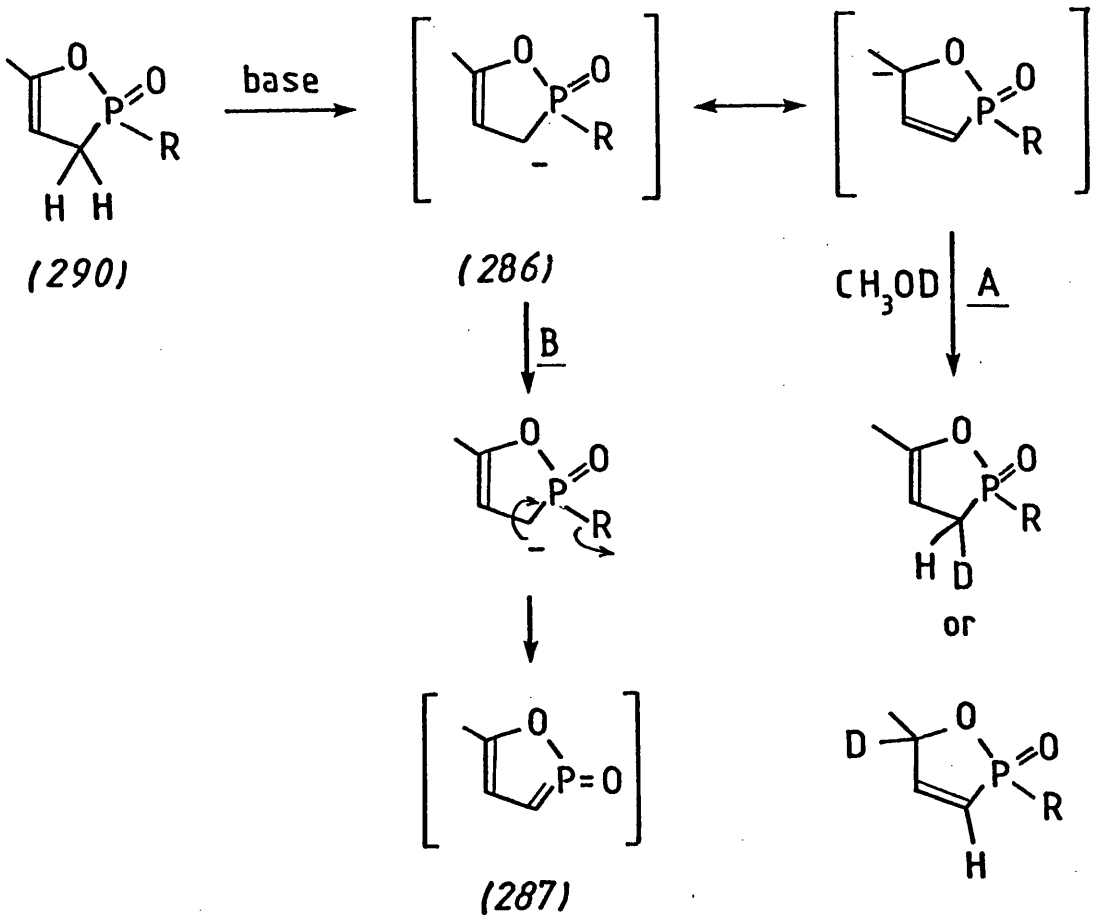
The analogous compound 2-ethoxy-4,5-benzo-1,2-oxaphospho1-3-ene *(283)*, can be synthesised by the method of Ivanov [120]. Salicyl alcohol (2-hydroxybenzyl alcohol) reacted with trialkyl phosphite to give a 'quasi'-phosphonium salt *(284)*. This rapidly converted to the phosphonate *(285)* which decomposed by an Arbuzov type reaction to give *(283)*.



(284) (283) (285)

Reactions of 1,2-oxaphospholenes

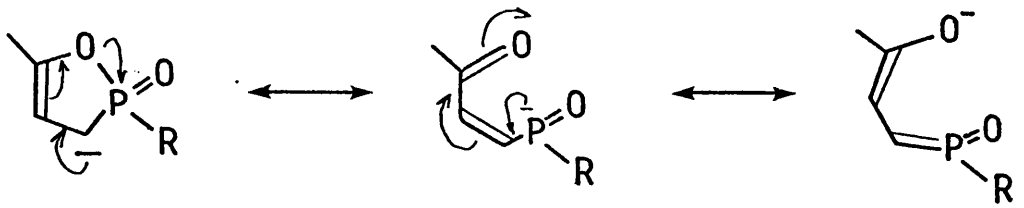
Attempts were made to remove one of the hydrogen atoms adjacent to phosphorus, in a number of 2-substituted-1,2-oxaphosphol-3-enes. The reactive species formed *(286)* could then react in two ways depending upon the nature of the 2-substituent.



If R was a good leaving group, such as a halogen, then *(286)* would follow pathway B. On the other hand, if R was a poor leaving group such as ethoxide or alkyl then pathway A would be favoured. Species similar to *(287)* have already been observed in the mass spectra of a number of 1,2-oxaphospholenes.

A third alternative to these routes is the ring-opening of *(286)* to

form the new anions *(288)* or *(289)*.



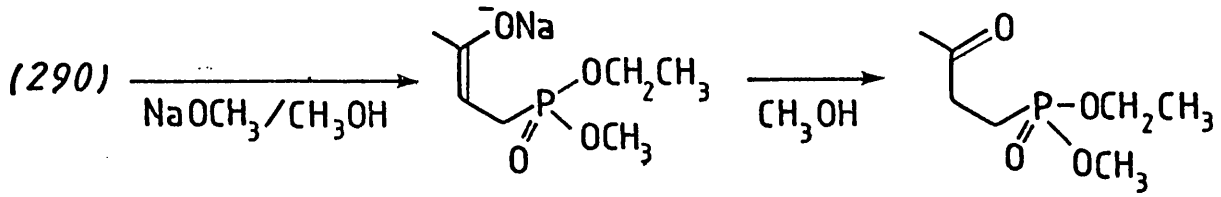
(288) *(289)*

The choice of a base to carry out these reactions is crucial. It must be non-nucleophilic, as attack at phosphorus followed by ring opening is a known reaction of 1,2-oxaphospholans [118], yet it must be a strong enough base to remove one of the hydrogen atoms.

When sodium methoxide in methanol was used the salt *(291)* was obtained. Addition of methanol caused the formation of the ethyl methyl (butan-3-one)phosphonate *(292)*.

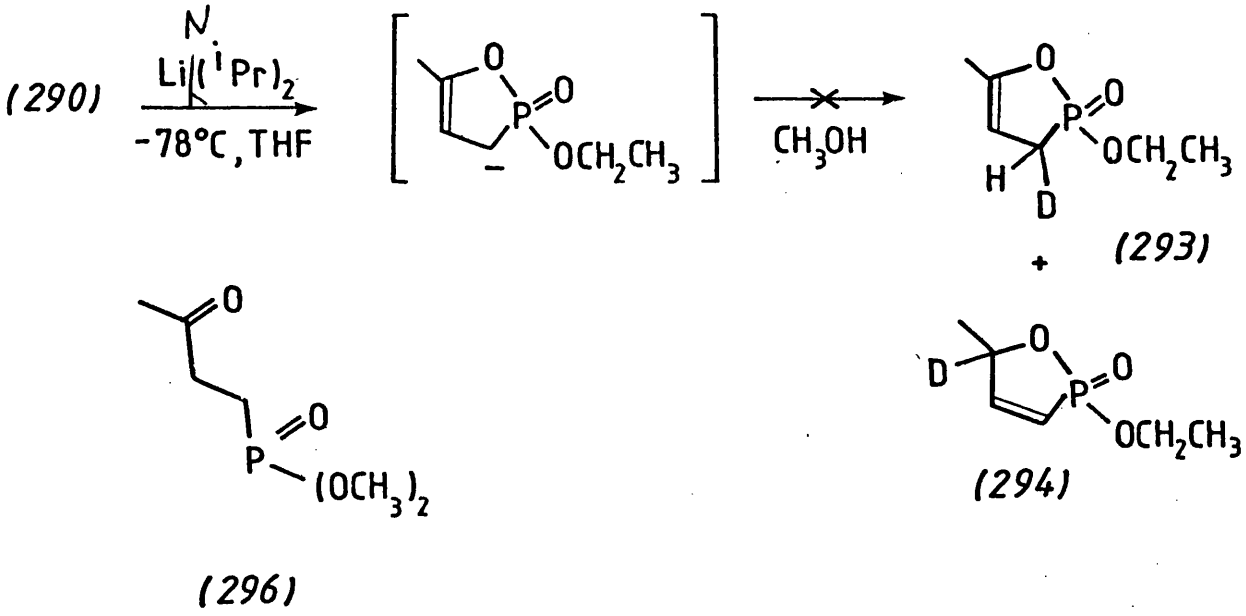
The reaction between *(290)* ($R = OCH_2CH_3$) and lithium diisopropylamide followed by the addition of deuteromethanol did not give the expected isomeric products, *(293)* and *(294)*. The reaction was monitored by ^{1}H and ^{31}P n.m.r. and no obvious products were identified.

When the same reaction conditions were applied to 2-chloro-5-methyl-1,2-oxaphosphol-3-ene *(295)* then the product identified by ^{1}H and ^{31}P n.m.r. was dimethyl-1-(butan-3-one)phosphonate *(296)*. Interestingly, there was no incorporation of deuterium atoms into *(296)*; this can be explained in terms of a ring opening by the first mole of deutero-methanol then displacement of the chloride ion with methoxide, the deuterium atoms always being present as -OD and therefore exchangeable.



(291) (292)

A number of attempts were made to use the species *(286)* (R = $-OCH_2CH_3$) to form non-conjugated ketones via a modified Horner-Emmons reaction [119], such reaction normally involving the very similar compounds of general formula *(299)*.



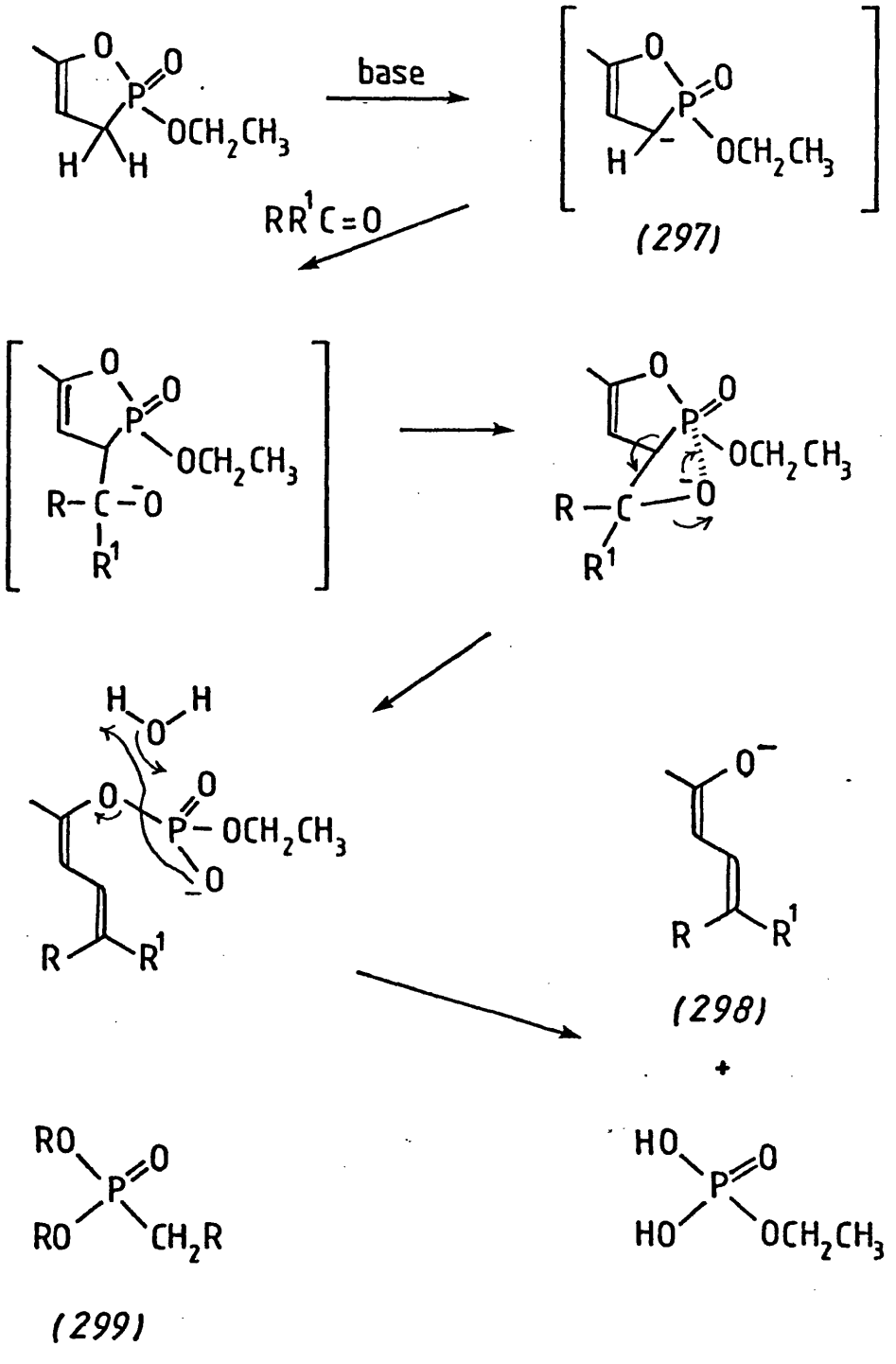
The reaction involved stirring the base in THF at -78°C and adding n-butyl lithium to form the lithium salt of the base, *(290)* (R = $-OCH_2CH_3$) was then added to give *(297)*. The addition of benzaldehyde was an attempt

to prepare 1-phenyl-pentɐn-4-one *(298)* (R= Ph, R= H) by the route shown.

A number of bases were used to prepare the anion *(297)*, these included t-butyl lithium, lithium diisopropylamide and lithium hexamethyldisilazane.. The general procedure for these reactions was firstly generation of the bases in the reaction flask, addition of *(290)* ($R = OCH_2CH_3$) and finally the trapping agent, benzaldehyde. The reaction mixture was then quenched with dilute acid and the products extracted with organic solvent and separation was by column chromatography. During this work it was expected that the ketone *(298)* would be isolated, however the only products obtained were benzaldehyde and, in some cases, diisopropylamine.

As the work with 1,2-oxaphosphol-3-enes proceeded no evidence emerged supporting the formation of the species *(297)*, although the reaction conditions would certainly have produced this moiety if either of the α-hydrogens were sufficiently acidic. The Horner-Emmons reaction uses compounds such as *(299)*, which are very similar to 1,2-oxaphosphol-3-enes. As formation of α-carbanions are possible for these compounds *(299)* there must be something preventing similar reactions for compounds *(290)*. Clearly the fact that the α-hydrogen atoms are not only adjacent to phosphorus but are also adjacent to an alkoxy-allyl grouping must make them more acidic. Also as the double bond is in conjugation to these protons, a driving force for such a reaction is the formation of a six-π electron system. The 1,2-oxaphosphol-3-ene molecules are very susceptible to ring opening and it may be that during the reaction or the work-up the unreacted compounds are being ring opened or, less likely, being converted by hydrolysis to water soluble materials which are neither isolated nor identified.

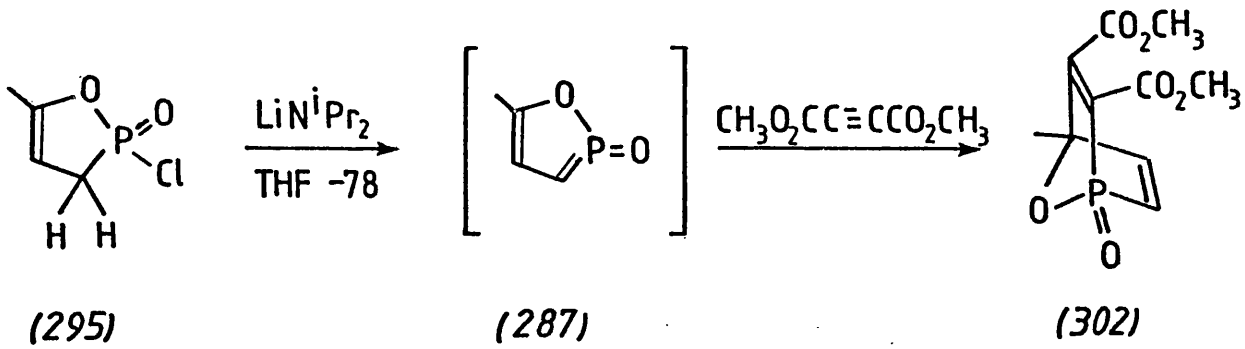
When *(295)* was treated with lithium diisopropylamide in the usual


base
RR¹C=O
(297)
(298)
+
(299)

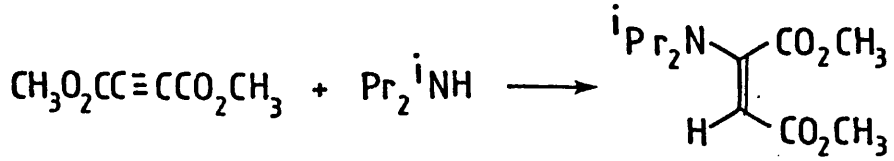
way, followed by the addition of a molar equivalent of dimethyl acetylenedicarboxylate the reaction did not proceed as expected but instead gave the dimethyl ester of diisopropylaminomaleic acid *(300)*.

The same product was obtained when the reaction was repeated in the absence of *(295)* and butyl lithium. Thus although *(295)* contains a good leaving group, it seems likely that α-hydrogen removal would produce a dienyl species *(287)* capable of being trapped by the acetylene, as no such reaction occurs it must be concluded that the reaction is not proceeding as hoped but a ring opening reaction is occurring.

The reaction of amines and acetylenedicarboxylic acid esters has already been reported in the literature [123,124].



(295) *(287)* *(302)*



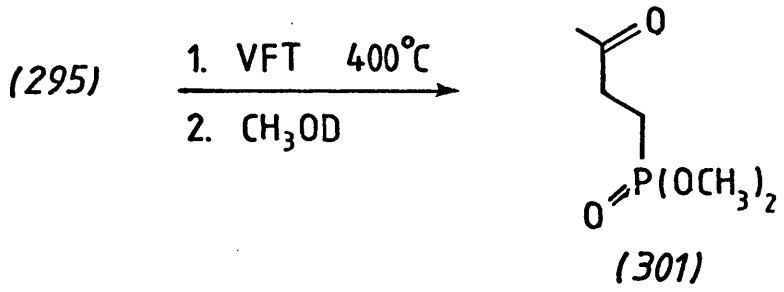
60%

(300)

Vacuum flash thermolysis (VFT) is a technique which often produces products that are observed in the mass spectrum of the parent molecule.

It is particularly useful when these products are very reactive and normally cannot be obtained by other means. The chloride *(295)* was placed in the VFT apparatus at a number of temperatures in an attempt to form *(287)*, which would have been 'sandwiched' between two layers of trapping reagent on the cold finger.

An experiment at 400°C using deuteromethanol in the trap of the apparatus, produced dimethyl (butan-3-one)phosphonate *(301)*. This can be rationalised as being unchanged *(295)* which is not being trapped but was reacting with the deuteromethanol when the cold finger was warmed up to room temperature.



(301)

When *(295)* was passed down the apparatus at 700°C with dimethyl acetylenedicarboxylate as the trapping agent then only the starting materials were isolated. A reaction did occur, however, when this experiment was repeated at 900°C although the product (^{31}P n.m.r. -48 p.p.m.) was not identified, because it could not be extracted from the reaction mixture.

When VFT reactions are carried out at these elevated temperatures unusual products can result, and it seems in this case the product obtained was not the expected material *(302)*.

In conclusion although mass spectral evidence exists to suggest that the formation of *(287)* might be possible, attempts to prepare it have been unsuccessful, both by the use of non-nucleophilic bases and by VFT.

EXPERIMENTAL

EXPERIMENTAL

Instrumentation

Infra-red spectra were recorded on Perkin-Elmer 237 or 580 spectrometers as dichloromethane solutions or thin films. Mass spectra were determined with an A.E.I. or a V.G. Micromass 16B instrument, with a gas chromatograph attachment. In each case, the molecular ion is given first, followed by peaks of structural significance. ^{1}H nuclear magnetic resonance spectra were recorded on a Varian T60 instrument with a locking facility, using deuterochloroform $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. 100 MHz ^{1}H n.m.r. spectra were recorded on a JEOL PS100 instrument.

Fourier-transform ^{31}P n.m.r. spectra were recorded on a JEOL FX60 instrument with TMS as internal standard. Some ^{31}P chemical shifts were determined by heteronuclear INDOR spectroscopy using an HD-60 heteronuclear decoupler linked to a Varian T60 spectrometer. ^{31}P n.m.r. chemical shifts are quoted relative to external 85% phosphoric acid.

Melting points were determined on a Kofler heating stage and are uncorrected. Gas chromatography was carried out using a Pye Unicam 104 chromatograph or 105 preparative chromatograph using nitrogen as the carrier gas and flame ionisation detectors.

General Details

All operations involving air or moisture sensitive compounds were carried out under an atmosphere of dry, oxygen-free nitrogen.

Small scale distillation and sublimations were carried out using a Kugelrohr oven and the boiling points, etc. quoted are the oven

temperatures at which the distillation occurred.

Diethyl ether and hydrocarbon solvents were dried over sodium wire, then distilled before use. Tetrahydrofuran was refluxed over and distilled from lithium aluminium hydride. Alcohols were refluxed over and distilled from their magnesium alkoxides. Dichloromethane, trichloromethane and tetrachloromethane were refluxed over and distilled from calcium hydride. All amines were dried by refluxing over, distilling from and storing over potassium hydroxide pellets. Acetonitrile was dried and fractionally distilled from P_2O_5.

All other liquid reagents and solvents were distilled before use.

Column chromatography was with either U.G.1 alumina or M.F.C. silica. In some cases, keiselgel 80 PF_{254} supplied by E. Merck was used, with the solvent under slight positive pressure.

Photolyses were carried out in a Rayonet photochemical reactor fitted with lamps emitting light of the required wavelength. The solutions were contained in quartz tubes (25 ml) and all solvents were degassed immediately before use.

N-bromosuccinimide was recrystallised from 10 times its volume of hot water then dried over P_2O_5 under vacuum overnight. Brominations were carried out using a quartz halogen spot lamp.

Mercuric acetate was recrystallised from acetic acid then dried over P_2O_5 under vacuum.

Details of the thermolysis apparatus and a description of a typical run

In flash vacuum thermolysis [146] (FVT) the compound under study is heated until in the gas phase. It is then passed down a very hot tube at low pressure. The products of the reaction being trapped on the cold finger at the end of the tube.

The contact times during which energy is transferred to the system are very short, normally between 1 and 20 ns. This enables a large proportion of the reactive intermediates formed to be trapped before they have time to react further within the furnace. That is, generally each molecule only strikes the hot surface once.

The contact time of the molecules within the system is given by the formula:

$$T = 0.16 \frac{Vr.P.t.}{Tr.M.}$$

where Vr is the volume of the hot zone; P - the pressure of the system; t - the time of the reaction in seconds; Tr - the temperature of the reaction, and M - the number of moles of material present.

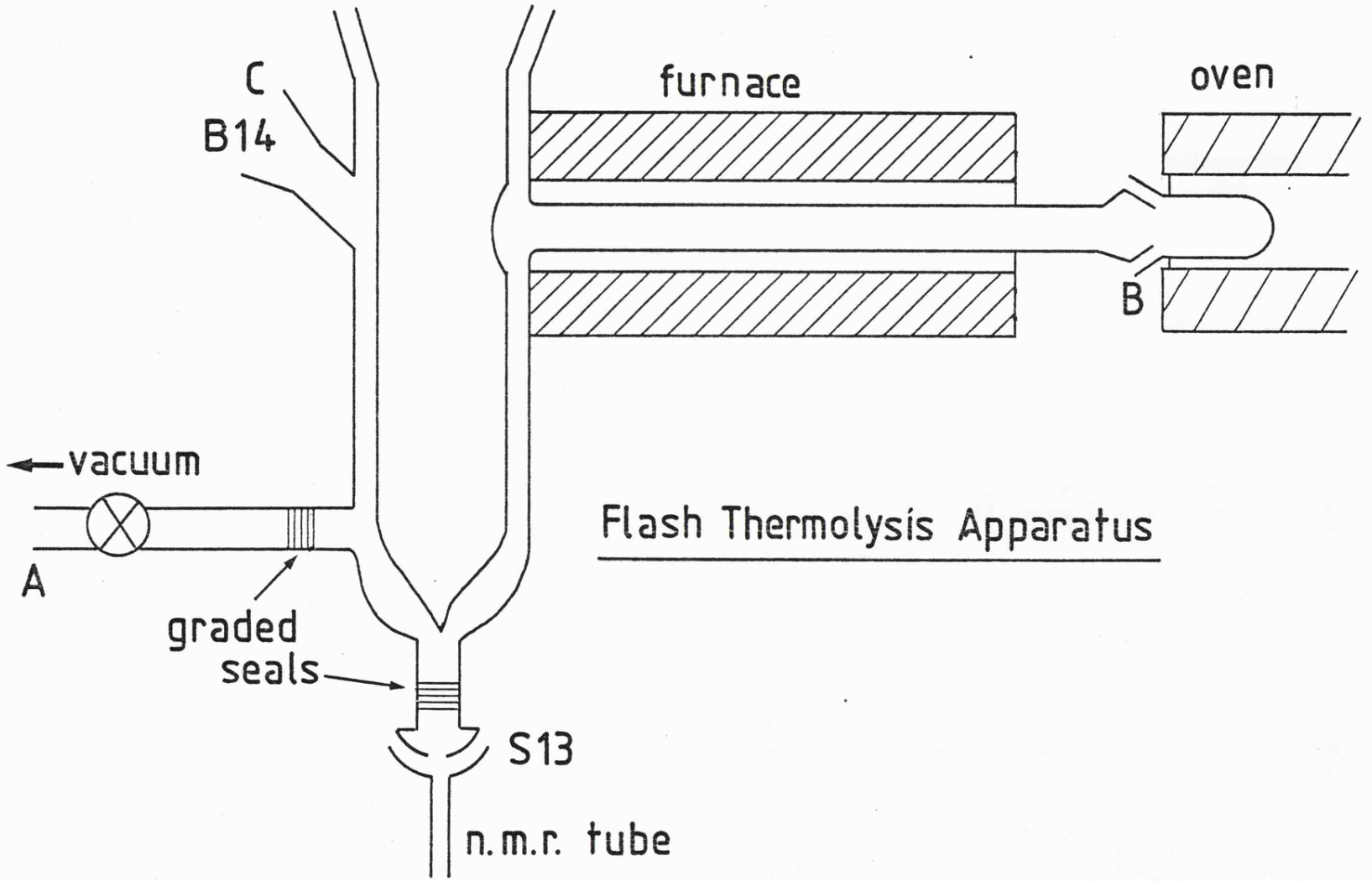
For preparative reactions the temperature of the furnace has to be kept as low as possible, without affecting the yield, so that the reactive intermediates are produced as near as possible to their ground state energies. If not, the products are more susceptible to undergo further reactions. To achieve these conditions the pressure must be as low as is practical, the cold trap must be as close as possible to the hot tube (approx. 13 mm was the actual distance) and the length of the hot zone has to be small (10 cm actual length).

The thermolysis apparatus, Diagram 1, was made of quartz glass, with the exception of the cold finger. The ball joint at the base of the equipment was capable of having either a round bottom flask (5 ml) or an n.m.r. tube attached, to collect the sample. The cold finger was cooled with a dry ice-acetone mixture to -78°C.

During a normal run, the apparatus was connected to an oil diffusion pump attached at 'A', and evacuated to approx. 1×10^{-3} torr as measured by a McLeod gauge, between the pump and the trap. The sample, of

around 100 mg, was contained in a round bottom flask (10 ml) fixed at 'B', or, if a volatile liquid was used, it was placed in a glass U-tube and frozen with a cold bath (dry ice-acetone), until the furnace reached the desired temperature. The temperature of the hot zone was controlled with a variac, and continuously monitored with a thermocouple connected to a digital thermometer. The thermocouple was inserted between the wall of the furnace and the hot tube, so that it lay in the middle of the hot zone. The sample was slowly sublimed through the apparatus, by the use of a Kugelruhr oven placed externally over the flask; in the case of a solid sample or, if the sample was a volatile liquid, the U-tube was slowly allowed to warm up and the sublimation regulated by a cold bath. The products generally condensed in the dimple of the cold finger.

When the sublimation had finished the apparatus was allowed to cool, then the system was flushed with dry nitrogen. The trap was warmed to room temperature, then the cold finger rotated so that the dimple was facing the inlet port 'C'. An n.m.r. solvent could be used to wash the products into the collecting flask.



Flash Thermolysis Apparatus

EXPERIMENTAL CHAPTER ONE

Preparation of bis(diethylamino)phenylphosphine

This compound was prepared using the method of Ewart [45] in 77% yield, b.p. 111-112°C at 0.8 mm Hg (lit. b.p. 91.5°C at 0.1 mm Hg, 70% yield), δ, 1.1 (t,12H,J=9Hz), 3.1 (Quartet, 8H,J=9Hz) and 7.1-7.5 (m, 5H).

Preparation of 2,3-diphenyl-1,3,2-oxazaphospholan

Prepared using the method of Mitsunobu [46] from bis(diethylamino)-phenylphosphine and N-phenylethanolamine (distilled before use 122-123°C at 1 mm Hg) in 82% yield, b.p. 159-160°C at 0.3 mm Hg (lit. b.p. 130-132°C at 0.03 mm Hg, 85%) [46], δ, 3.0-3.5 (m,2H), 3.7-4.6 (m,2H) and 6.5-7.5 (m,10H), $^{31}P(CDCl_3)$ -128 p.p.m.

Preparation of 3-methyl-2-phenyl-1,3,2-oxazaphospholan

This compound was prepared from bis(diethylamino)phenylphosphine and N-methylethanolamine (pre-distilled 65-66°C at 30 mm Hg) using the method of Mitsunobu [46], b.p. 86-90°C at 0.04 mm Hg, 32% yield (lit. b.p. 88-91°C at 0.02 mm Hg, 25%), δ, 2.8 (d,5H,J=14Hz, two hydrogen atoms of the ring appear under this doublet), 3.9-4.2 (m,2H) and 7.2-7.4 (m,5H).

Preparation of N-chlorodiisopropylamine

Prepared using the method of Block and Kompa [47] b.p. 36-38°C on a water pump (lit. b.p. 40°C, water pump, 58%), δ, 1.2 (d,12H,J=8Hz) and 3.2 (Septet, 2H,J=8Hz).

Preparation of 9-methyl-5-phenyl-2,3-benzo-9-aza-1,4,6-trioxa-5-phosphaspiro-[4,4]-nonane

2-Methyl-3-phenyl-1,3,2-oxazaphospholan (4.9g, 27 mmols) was dissolved in ether (100 ml), placed in a 3-necked round bottomed flask (250 ml) and cooled to -78°C under nitrogen. An equimolar amount of pyrocatechol (2.89g, 27 mmols) was added. N-chlorodiisopropylamine (freshly prepared, 3.39g, 27 mmols) in ether (50 ml) was then added dropwise to the rapidly stirred solution, a white precipitate formed. After the addition the mixture was stirred for 30 min. at this temperature then allowed to warm up to room temperature and stirred overnight. After filtration through filter aid under nitrogen the ether was removed under reduced pressure. White crystals of 9-methyl-5-phenyl-2,3-benzo-9-aza-1,4,6-trioxa-5-phosphaspiro-[4,4]-nonane (6.5g, 83%).

The product was recrystallised from 60-80°C petrol, m.p. 94-96°C, $\nu_{max.}$ (nujol mull), 2950(bd), 1620, 1600, 1490, 1450, 1440, 1360, 1250, 1235, 1220, 1180, 1120, 1100, 1070, 1040, 1010, 960, 870, 850, 780, 740 and 720, δ, 3.1 (d,2H,J=10Hz), 2.8-3.5 (m,2H), 3.5-4.2 (m,2H), 6.6-7.0 (m,4H) and 7.1-7.8 (m,5H), m/e (13eV) 290(m+1), 289(m^+), 246, 245, 234, 233, 232, 217, 216, 215, 186, 181, 180, 178, 139, 110, 104, 92, 91, 80, 77, 57, u.v. (methanol) ε_{217nm}=5491 and ε_{275nm}=4017 , $C_{15}H_{16}O_3NP$, Expect: C, 62.28; H, 5.54; N, 4.84; P, 10.75. Found: C, 62.53; H, 5.69; N, 5.05; P, 10.52; $^{31}P(CDCl_3)$ + 30 p.p.m.

Preparation of 5,9-diphenyl-2,3-benzo-9-aza-1,4,6-trioxa-5-phosphaspiro-[4,4]-nonane

2,3-Diphenyl-1,3,2-oxazaphospholan (4.0g, 16 mmols) was dissolved in ether (50 ml) and placed in a flask at -78°C. An equimolar amount of pyrocatechol (1.8g, 16 mmols) was then added. N-chlorodiisopropylamine

(freshly prepared, 2.2g, 16 mmols) in ether (10 ml) was introduced dropwise to the rapidly stirred solution, a white precipitate formed. After 30 min. the flask was allowed to warm up to room temperature and stirred overnight. Filtration through filter aid in the presence of nitrogen and removal of the solvent under vacuum gave white crystals of 5,9-diphenyl-2,3-benzo-9-aza-1,4,6-trioxa-5-phosphaspiro-[4,4]-nonane in (3.1g, 55%) yield. The product was recrystallised from 60-80°C petrol. (A small amount of oxide present) melts with decomposition at 68°C and above, $\nu_{max.}$ (nujol mull), 2900(bd), 2720, 2680, 1600, 1480, 1450(bd), 1370, 1350, 1340, 1300, 1280, 1250, 1150, 1080, 970, 940, 900, 850 and 720, δ, 3.3-4.6 (m,4H), 6.1-7.9 (m,14H), m/e 352(m+1), 351(m^+), 325, 324, 259, 258, 238, 234, 233, 232(100%), 217, 216, 215, 214, 186, 169, 168, 139, 120, 119, 118, 110, 107, 106, 105, 92, 91, 80, 78, 77, u.v. (methanol), ε_{217nm}=5965, ε_{275nm}=2246, ^{31}P ($CDCl_3$) + 33 p.p.m., $C_{20}H_{18}O_3NP$, Expect: N, 3.99; P, 8.83; H, 5.13; Found: N, 3.92; P, 8.55; H, 5.47.

Preparation of N-β-bromoethylaniline hydrobromide

This compound was prepared using the method of Pearlman [48] from β-hydroxyethylaniline and hydrobromic acid in 34% yield, m.p. 136-138°C, 85%, δ, 3.7 (s, $-CH_2CH_2-$ protons).

Preparation of N-phenylaziridine

Using the method of Heine [49], N-phenylaziridine was obtained in 54% yield, b.p. 69-70.5°C at 13 mm Hg, 68%, δ, 2.0 (s,4H), 6.7-7.3 (m,5H).

Preparation of 2,2-dihydro-4,5-diphenyl-2,2,2-trimethoxy-1,3,2-dioxaphospholan

The compound was prepared using the method of Ramirez [50], m.p.

46-48°C in 63% yield (lit. m.p. 47-49°C, in quantitative yield), δ, 3.95 (d,9H,J=14Hz) and 7.4-8.0 (m,10H).

Preparation of 2,2,3,4,4-pentamethyl-1-phenylphosphetan

2,2,3,4,4-Pentamethyl-1-phenylphosphetan 1-oxide (10g, 42 mmols a 50/50 mixture of cis and trans isomers) was added to silicone fluid (10 ml, M.S. 1107) and slowly heated to 140°C. After 1h. the lumps of the product were broken up and it was distilled from the flask. 2,2,3-4,4-Pentamethyl-1-phenylphosphetan (5.8g) was obtained in 62% yield.

Preparation of the 2,2,3,4,4-pentamethyl-1-phenylphosphetan/9,10-phenanthraquinone adduct

9,10-Phenanthraquinone (5.5g, 26 mmols, sublimed before use) in dichloromethane (20 ml) was added dropwise to a stirred solution of 2,2,3,4,4-pentamethyl-1-phenylphosphetan (5.6g, 25 mmols) in dichloromethane (25 ml) at 0°C under nitrogen. After the exothermic reaction had subsided the solution was refluxed for 2h. The solvent was then removed under vacuum to give the 2,2,3,4,4-pentamethyl-1-phenylphosphetan/9,10-phenanthraquinone adduct. Recrystallisation from ethyl acetate gave a yellow crystalline product (5.4g, 50% yield, after first crystallisation), δ, 0.8-1.9 (m,16H), 7.2-8.2 (m,11H) and 8.6-8.9 (m,2H), u.v. (acetonitrile, benzene free), ε_{223nm}=70192, ε_{254nm}=81320, ε_{260nm}=89024, ε_{276nm}=71904, ε_{325nm}=20544, $^{31}P(CDCl_3)$ -9 and -2 p.p.m. (lit. ^{31}P cis -7.7 p.p.m., trans +0.02 p.p.m. [o-dichlorobenzene]), 72% and 28% respectively.

$\nu_{max.}$ (CH_2Cl_2 solution) 3120, 3040, 2950(bd), 1650, 1620, 1610, 1460, 1380, 1340, 1120, 1110, 1060, 1030, 960 and 900 cm^{-1}.

Thermolysis of 5,9-diphenyl-2,3-benzo-7-aza-1,4,6-trioxa-5-phosphaspiro-[4,4]-nonane

5,9-Diphenyl-2,3-benzo-9-aza-1,4,6-trioxa-5-phosphaspiro-[4,4]-nonane (89.8 mg, 0.25 mmols) was placed in an n.m.r. tube and heated at 120°C for 20 min., deuterochloroform was added and an n.m.r. spectrum recorded, δ, 3.4 (s), 4.2-4.6 (m) and 6.3-8.0 (m). Attempts to distil the phosphorane led to similar products (120°C at 0.03 mm Hg) $^{31}P(CDCl_3)$ -36 (45%), -27 (3%), -20 (21.5%), -19 (2%), -15 (20%), +10 (5.5%), +33 (3%) p.p.m. G.L.C. 3% OV 17 at 250°C, N_2 = 10 psi, 1 min/cm, 0.2μl injection, R_t; 0.4 (solvent) min., 0.7 min., 5.1 min. (major peak), and 11.5 min., also two very minor peaks at 1.1 and 2.0 min.

Photolysis of 5,9-diphenyl-2,3-benzo-9-aza-1,4,6-trioxa-5-phosphaspiro-[4,4]-nonane

5,9-Diphenyl-2,3-benzo-9-aza-1,4,6-trioxa-5-phosphaspiro-[4,4]-nonane (250 mg, 0.7 mmols) was dissolved in methanol (degassed, 25 ml) and irradiated with ultra-violet light (λ = 254nm) for 3h. The solvent was removed under reduced pressure, δ, 3.45 (s), 3.0-3.4 (bd,s), 3.7 (d,J=10Hz), 6.1 (bd,s), 6.3-7.8 (m). G.L.C. 3% OV 17, 250°C, N_2 = 10 psi, 1 min/cm, 0.2μl injections, R_t = 0.5 (solvent) min., 0.9, 1.0 (minor), 1.2 (major), 5.8 and 11.7 min.

The vacuum flash thermolysis of 9-methyl-5-phenyl-2,3-benzo-9-aza-1,4,6-trioxa-5-phosphaspiro-[4,4]-nonane

9-Methyl-5-phenyl-2,3-benzo-9-aza-1,4,6-trioxa-5-phosphaspiro-[4,4]-nonane (314 mg, 1.1 mmols) was placed in the vacuum flask apparatus. Furnace 750°C, pressure 0.025 mm Hg, oven 150°C, δ, 2.7 (d,J=10Hz), 3.2 (d,J=10Hz), 3.4-4.8 (m), 6.8-8.2 (m). G.L.C. 3% OV 17, 200°C, N_2 = 10 psi, H_2 = 14 psi, air = 12 psi, 0.2μl, 1 cm/min., R_t = 0.6, 1.4, 2.6, 3.8 and 7.2 min., $^{31}P(CDCl_3)$ -36 (13.5%), -33 (35%), -18 (5.5%),

-16 (24%) and +30 (22%) p.p.m.

Photolysis of 2,2,3,4,4-pentamethyl-1-phenylphosphetan/9,10-phenanthraquinone adduct

2,2,3,4,4-Pentamethyl-1-phenylphosphetan/9,10-phenanthraquinone (292 mg, 0.7 mmols) was dissolved in acetonitrile (24 ml) and methanol (6 ml). The solution was degassed for 1h. then irradiated with ultra-violet light, the reaction being followed by thin layer chromatography. After 60h. the solvent was removed under reduced pressure to give 250 mg of photolysis products. $^{31}P(CDCl_3)$, -65 (12%), -61 (36%), -57 (45%), -27 (7%) p.p.m. The products were separated by column chromatography on alumina (UG1, 10g, ether increasing in polarity to 2% methanol), the only products isolated were trans-2,2,3,4,4-pentamethyl-1-phenylphosphetan 1-oxide, δ, $CDCl_3$; 1.05 (s), 1.45 (s) and 1.75 (15H) and 7.2-8.35 (m,5H), (lit. m.p. 126-127°C lit. ^{31}P = -57 p.p.m.), cis-2,2,3,4,4-pentamethyl-1-phenylphosphetan 1-oxide, δ, $CDCl_3$; 1.2 (s), 1.4 (s), 1.45 (s), 1.5 (s) and 1.6 (s), (lit. m.p. 117-118°C, lit. ^{31}P = -56 p.p.m.).

Photolysis of 2,2,3,4,4-pentamethyl-1-phenylphosphetan/9,10-phenanthraquinone adduct in methanol

2,2,3,4,4-Pentamethyl-1-phenylphosphetan/9,10-phenanthraquinone adduct (478 mg, 1.1 mmols) was dissolved in methanol (30 ml) and degassed for 1h. The solution was placed in the dark at room temperature for 40h. The solvent was removed under reduced pressure, 420 mg (88% recovery) of starting material.

A sample of 2,2,3,4,4-pentamethyl-1-phenylphosphetan/9,10-phenanthraquinone adduct (565 mg, 1.3 mmols) was dissolved in methanol (30 ml) and degassed for 1h. The solution was photolysed with ultra-violet light (λ = 254nm) for 41h., an orange precipitate (216 mg, 38%) had

formed (m.p. 195-195.5°C, lit. m.p. [51] for 1-phenyl-2,2-trans-3,4,4-pentamethylphosphetan/9,10-phenanthraquinone = 195°C). The solvent was removed under vacuum and identified as a mixture of cis and trans-2,2,-3,4,4-pentamethyl-1-phenylphosphetan 1-oxide.

Attempted thermolysis of 4,5-diphenyl-2,2,2-trimethoxy-1,3,2-dioxaphospholan

4,5-Diphenyl-2,2,2-trimethoxy-1,3,2-dioxaphospholan (1g, 3 mmols) was placed in a flask under nitrogen and heated at 200°C for 18h. The reaction was followed by gas chromatography (3% OV 17, 250°C, N_2 = 43 ml/min., 1 cm/min. 0.2µl) after 5h. the starting material was still present (R_t 2.6 min.). After 18h. all the starting material had reacted and been converted into benzil (7.2 min.), $(MeO)_3P$ (0.6 min.) and a small amount of $(MeO)_3P=O$ (0.4 min.).

Thermolysis in presence of naphthalene

The gas chromatographic conditions were the same as for the above reactions, naphthalene had a retention time of 1.25 min. 2,2-Dihydro-4,5-diphenyl-2,2,2-trimethoxy-1,3,2-dioxaphospholen (1g, 3 mmols) was placed in a flask under nitrogen with an excess of naphthalene (1g, 7.8 mmols) and heated at 200°C for 18h. G.L.C. shows the presence of a small amount of starting material. The major products were benzil and trimethyl phosphite. Column chromatography on alumina (U.G.1., eluted with petrol/ether) isolated benzil, unreacted naphthalene and a number of hydrolysis products derived from $(MeO)_3P$ and $(MeO)_3PO$.

Photolysis of 4,5-diphenyl-2,2,2-trimethoxy-1,3,2-dioxaphosphol-3-ene in methanol

4,5-Diphenyl-2,2,2-trimethoxy-1,3,2-dioxaphosphol-3-ene (292 mg, 0.9 mmols) in methanol (25 ml, degassed for 1h.) was photolysed (λ = 254nm)

for 24h. The reaction was monitored by gas chromatography (3% OV 17, 200°C 1 cm/min., N_2 = 8 psi, 0.2µl) the products identified were $(MeO)_3P=O$ (R_t = 48 s., compared with authentic sample) and benzil ($R_t = 9\frac{1}{4}$ min.). Another peak was identified as 2,3,5,6-tetraphenyl-1,4-oxe-2,5-diene (m/e 195, 194, 100%), 165 and 119 with a meta-stable peak at 140 (either 194 → 165 or 388 → 234). One peak was not identified.

Dark reaction

4,5-Diphenyl-2,2,2-trimethoxy-1,3,2-dioxaphosphol-3-ene (125 mg, 0.37 mmols) was dissolved in methanol (25 ml, degassed) and the solution degassed for 40 min. The solution was then placed in the dark at room temperature for 3h. After removal of the solvent, the products identified were $(MeO)_3P$, and benzil.

Vacuum flash thermolysis of 4,5-diphenyl-2,2,2-trimethoxy-1,3,2-dioxaphosphol-3-ene

At 600°C

4,5-Diphenyl-2,2,2-trimethoxy-1,3,2-dioxaphosphol-3-ene (0.7g, 2 mmols) was placed in the vacuum flash thermolysis apparatus under nitrogen (furnace 600°C, oven rising to 125°C over 1h., 0.06 mm Hg). The products were washed off the cold finger with $CDCl_3$/TMS. Products identified were benzil and trimethyl phosphite (plus the two minor impurities appearing in a later thermolysis.

At 750°C

4,5-Diphenyl-2,2,2-trimethoxy-1,3,2-dioxaphosphol-3-ene (2.43g, 7 mmols) was placed in the vacuum flash thermolysis apparatus under nitrogen (furnace 750°C, over 200°C, 0.06 mm Hg). The products were washed off the cold finger with $CDCl_3$/TMS. Thermolysis products (2.2g) were obtained in 91% (leaving a residue of 168 mg (6.7%) as a red oil

and identified as benzil, trimethyl phosphite (57% of phosphorus containing products) and dimethyl methylphosphinate $[Me-\overset{O}{\overset{\|}{P}}(OMe)_2]$ (43%). No $(MeO)_3P=O$ was present.

EXPERIMENTAL CHAPTER TWO

Preparation of 2,3-diphenylbuta-1,3-diene

Prepared by the method of Org. Syn. VOL. 50, p.62, from DMSO, sodium hydride and phenylacetylene m.p. 57-58°C in 13% yield (lit. m.p. 47-48°C yield 13%).

Reactions of 2,3-diphenyl-1,3,2-oxazaphospholan

Dark reaction with methanol

2,3-Diphenyl-1,3,2-oxazaphospholan (60 mg, 2.5×10^{-4} moles) was dissolved in methanol (dried, distilled and degassed, 25 ml) and degassed for a further 40 min. The quartz tube holding the solution was placed in the dark for 2 days. ^{31}P n.m.r. -160 p.p.m. (93%) plus a small peak at -29 p.p.m. (7%). The same sample was then exposed to the light for a further 2 days, ^{31}P n.m.r. -29 p.p.m. The peak at -160 p.p.m. was identified as dimethyl phenylphosphinate.

Photolysis in methanol

2,3-Diphenyl-1,3,2-oxazaphospholan (194 mg, 0.8 mmols) was dissolved in methanol (20 ml, dry, distilled and degassed) the solution was degassed for 30 min. Photolysis ($\lambda = 254$nm) for 1h. showed starting material to still be present, after a further hour's irradiation the products were identified as 2-anilinoethanol, methyl phenylphosphinate (^{31}P n.m.r. -27 p.p.m.) δ, ($CDCl_3$), 2.8 (s) and 12.8 (s,1H, P-H coupling), 3.2-3.4 (q), 3.5 (s) (diphenylpiperazine), 3.8 (d,J=14Hz) (P-OCH_3 doublet), 4.4-4.8 (m), 6.6-8.2 (m);

and dimethyl phenylphosphonite (^{31}P n.m.r. -160 p.p.m.).

Dark reaction with acetonitrile

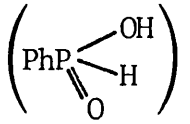
2,3-Diphenyl-1,3,2-oxazaphospholan (162 mg, 0.66 mmols) was

dissolved in acetonitrile (15 ml) and degassed for 40 min. Isoprene (1 ml, 10 mmols) (freshly distilled) was added and the sample placed in the dark. After 24h. the sample (5 ml) contained mainly starting material (^{31}P n.m.r. -128 p.p.m.).

Photolysis in acetonitrile (in the presence of isoprene)

2,3-Diphenyl-1,3,2-oxazaphospholan (216 mg, 0.9 mmols) and isoprene (1 ml) were dissolved in degassed acetonitrile (15 ml) and the solution photolysed for 2h. The solvent was then removed under vacuum. The products were identified by ^{1}H n.m.r. and ^{31}P n.m.r. to be mainly starting material and its oxide. ^{31}P n.m.r. -128 p.p.m. (42%), -27 p.p.m. (oxide) (20.9%) and three minor peaks -26 p.p.m. (19.2%), -23 p.p.m. (11.2%) and -22 p.p.m. (6.7%).

Photolysis of the remainder of the 'dark run' solution for 18h. (in the presence of isoprene) gave a ^{31}P n.m.r. spectrum containing peaks at -37 p.p.m. (5%), -27 p.p.m. (25.8%), -26 p.p.m. (58.7%) and -16 p.p.m. (10.5%). A thick layer chromatograph had a base-line which when extracted from the plate contained a product with a ^{31}P n.m.r. of -19 p.p.m. (92 mg, a 43% recovery), probably phenylphosphinate



Photolysis in dichloromethane (in the presence of 2,3-diphenylbuta-1,3-diene)

Dichloromethane (15 ml, dry, dist.) was degassed for 40 min., then 2,3-diphenyl-1,3,2-oxazaphospholan (156 mg, 0.6 mmols) was dissolved in it, with 2,3-diphenylbuta-1,3-diene (132 mg, 0.6 mmols) and the solution photolysed, (λ = 254nm). The reaction was followed by t.l.c. on silica and alumina. After 113h., ^{31}P n.m.r. ($CDCl_3$) -19 p.p.m.

Thermolysis in o-dichlorobenzene

2,3-Diphenyl-1,3,2-oxazaphospholan (415 mg, 1.7 mmols) was placed in a flask under nitrogen with 2,3-diphenylbuta-1,3-diene (354 mg, 1.7 mmols) and o-dichlorobenzene (dry, distilled and degassed, 50 ml). The solution was then heated at reflux temperature for 2h. Starting material and its oxide were observed. After 8h. the proportion of oxide was slightly higher.

The above experiment was repeated with oxazaphospholan (436 mg, 1.8 mmols), diene (384 mg, 1.9 mmols) and o-dichlorobenzene (5 ml). The reagents were heated at 190°C for 3½h. then left to cool overnight, ^{31}P n.m.r. -15 p.p.m., solvent removed by distillation, δ, ($CDCl_3$) 1.45 (t,J=8Hz), 2.6-3.4 (b.s), 3.4-3.8 (m), 7.2-7.9 (m), 8.3 (b.s), 9.8 (b.s).

Vacuum Flash Pyrolysis (isoprene trap)

Isoprene (2 ml, freshly distilled) was placed in the U-tube of the vacuum flash pyrolysis apparatus used in Chapter 3. The isoprene was cooled in liquid N_2, as the vacuum was applied, then allowed to warm up to room temperature while passing through the apparatus and condensing on the cold finger. The vacuum was removed and the system filled with dry nitrogen. 2,3-Diphenyl-1,3,2-oxazaphospholan (150 mg, 0.6 mmols) was flashed through the apparatus, the oven at 120°C, the furnace at 800°C. Isoprene was sandwiched on top of the thermolysis products and the system allowed to warm up to room temperature. By ^{31}P n.m.r. ($CDCl_3$) -14 p.p.m. (58%) and 2,3-diphenyl-1,3,2-oxazaphospholan 2-oxide, -27 p.p.m. (42%) were obtained.

EXPERIMENTAL CHAPTER THREE

Preparation of methyl diphenylphosphinite

Prepared in good yield by the method of Arbuzov and Nikonorov [101], and used as a crude reaction mixture in the next preparation (lit. b.p. 1 mm Hg 110-115°C in 69% yield).

Preparation of diphenylbut-2-enylphosphine oxide

This compound was prepared using the method of Berlin [97]. Purification was by column chromatography on alumina, UG1, eluted with ethyl acetate, m.p. 108-109°C, lit. m.p. [97] 114-116°C.

Preparation of 4-methyl-1-phenyl-1,2,3,4-tetrahydrophosphinoline oxide

Diphenylbut-2-enylphosphine oxide (14.2g, 5.5 mmols) was dissolved in o-dichlorobenzene (100 ml) and added over 1h. to polyphosphoric acid (85%, 100 ml) and o-dichlorobenzene (300 ml) at 180°C, in a litre flask fitted with a reflux condenser and a mechanical stirrer. After the addition the mixture was heated for another 4h. at this temperature then cooled to 100°C. It was poured into three litres of ice/water and mechanically stirred overnight. The solution was then filtered and the product extracted with chloroform (4 ×500 ml). The combined organic fractions were washed with water and the chloroform pumped away under reduced pressure to give 4-methyl-1-phenyl-1,2,3,4-tetrahydrophosphinoline-1-oxide (8.5g, 3.3 mmols) in 60% yield. This compound was purified by column chromatography on alumina (UG1, 600g) packed in petrol and eluted with ether, increasing the polarity slowly to 5% methanol/ether. $\nu_{max.}$ (Film) 3060, 2960, 2930, 2870, 1605, 1575, 1485, 1465, 1445, 1415, 1290, 1200, 1170, 1150, 1120, 1090, 915, 895 and 750(b) cm^{-1}, δ, 1.3 (dd, 3H, J=4,8Hz), 1.6-2.6 (m,4H), 2.8-3.4 (broad s,

1HO), 7.1-7.9 (broad s, 9H), m/e 256 (m^+), 255, 242, 241, 228, 227, 216, 215, 202, 201, 179, 164, 117, 116, 115, 92 and 77. $^{31}P(CDCl_3)$ -25.7 (-24.8) p.p.m., $C_{16}H_{17}PO$; requires P 12.09, found 12.08.

Preparation of 1,3,3-triphenylphosphinoylpropan-1-ol

Diphenylmethylphosphine oxide (5.0g, 0.023 moles, made by the action of methyl magnesium iodide on diphenylphosphinoyl chloride [102,103]) in tetrahydrofuran (60 ml) under nitrogen, was treated with n-butyl lithium (16 ml of 1.5M n-buLi in hexane) at room temperature for 30 min. The solution (which changed from yellow to red in colour) was cooled to -78°C and styrene oxide (2.7g, 2.6 cm^3, 0.023 moles) was added as a THF (10 ml) solution. It was allowed to warm up to room temperature and stirred for 45 min., after which time it had become an orange solution. Saturated ammonium chloride solution (100 cm^3) was added to the reaction mixture and the aqueous layer extracted with dichloromethane (3 × 100 ml). The combined organic fractions were dried over magnesium sulphate, filtered, and the solvent removed under reduced pressure. The crude product (7.5g) was recrystallised from benzene to give white crystals of 1-phenyl-3-diphenylphosphinoylpropan-1-ol (5.5g, 72% yield), m.p. 146-147°C. $\nu_{max.}$ (CH_2Cl_2 solution) 3280, 3020, 2900, 1605, 1590, 1490, 1480, 1435, 1420, 1400(broad), 1170(broad), 1120, 1100, 1070, 1060, 1020, 990 and 890 cm^{-1}, δ, 1.8-2.3 (m,4H), 4.4 (broad s, 1H, -OH proton signal removed by D_2O shake), 4.9 (broad s, 1H), 7.3-8.0 (m,15H), m/e 337 (m+1), 336 (m^+), 335, 319, 318, 317, 306, 259, 231, 230, 229, 217, 216, 215, 203, 202, 201, 199, 193, 185, 184, 183, 155, 154, 153, 152, 133, 125, 117, 116, 115, 107, 105, 91, 79, 78 and 77, $C_{21}H_{21}O_2P$. Required C, 75.00; H, 6.25; P, 9.23; Found, C, 75.43; H, 6.37; P, 9.15.

Preparation of 1,2,2-triphenylphosphinoylbutan-1-ol

Diphenylethylphosphine oxide (4.5g, 0.02 moles, prepared by the action of ethyl magnesium bromide on diphenylphosphinoyl chloride) in tetrahydrofuran (50 ml) was treated with equimolar amounts of n-butyl lithium (13 ml of 1.5M n-buLi in hexane) and styrene oxide (2.35g, 2.2 cm^3, 0.02 moles) as previously described for 1,3,3-triphenylphosphinoylpropan-1-ol. The white product (6.5g) was recrystallised from benzene/petrol to give 1,2,2-triphenylphosphinoylbutan-1-ol (4.5g) in 66% yield, m.p. 175°C; $\nu_{max.}$ 3250(broad), 1605, 1595, 1490, 1440, 1420, 1190, 1165, 1120, 1100, 1075, 1050, 1030, 1000 cm^{-1}, δ, 1.25 (dd,3H,J=7 and 17Hz), 1.8-2.8 (m,3H), 4.8-5.1 (m,2H) and 7.2-7.8 (m,15H), D_2O shake collapses the multiplet at 5.08 to a triplet which then integrates to OMe proton, m/e 351 (m+1), 350 (m^+), 349, 348, 333, 332, 331, 305, 272, 271, 243, 242, 202, 201, 200, 182, 154, 153, 152, 130, 124, 123. Metastable peaks at 176, 166 and 118, $C_{22}H_{23}O_2P$ Requires C, 75.43; H, 6.57; P, 8.86, Found C, 75.27; H, 6.68; P, 8.75.

Preparation of 1,4-diphenyl-1,2,3,4-tetrahydrophosphinoline 1-oxide

Polyphosphoric acid (85% P_2O_5, 50 ml) was placed in a round bottom flask and heated to 100°C. 1,3,3-Triphenylphosphinoylpropan-1-ol (1g, 0.3 mmols) was added and the mixture then heated to 190°C for 4h. The reaction mixture was cooled to 110°C and poured with rapid stirring into ice-water (300 ml). The mixture was stirred until homogeneous (overnight) then the product was extracted with chloroform (3 × 50 ml). The organic fraction was washed with sodium hydrogen sulphate solution (100 ml, 10%) and then water (100 ml). The chloroform was dried over magnesium sulphate, filtered and removed under reduced pressure. 1,4-Diphenyl-1,2,3,4-tetrahydrophosphinoline 1-oxide was obtained as a pale

brown oil (550 mg) in 55% yield. Purification was by column chromatography on alumina (UG1, 25g) packed in petrol and eluted with ethyl acetate, δ, 1.8-3.0 (m,4H), 4.2-4.6 (m,1H), 7.0-8.1 (m,14H), m/e 319 (m+1), 318 (m^+), 317, 303, 302, 301, 256, 255, 254, 253, 252, 242, 241, 227, 215, 201, 191, 178, 166, 165, 140, 125, 115, 91, 83 and 81; $\nu_{max.}$ 2940, 2870, 1670, 1595, 1500, 1485, 1480, 1470, 1450, 1440, 1380, 1370, 1320, 1180 (broad), 1120, 1070, 1030 (broad), 950 cm^{-1}.

Preparation of 1,4-diphenyl-2-methyl-1,2,3,4-tetrahydrophosphinoline 1-oxide

Prepared using the same method as that for 1,4-diphenyl-1,2,3,4-tetrahydrophosphinoline 1-oxide by heating 1,2,2-triphenylphosphinoyl-butan-1-ol in polyphosphoric acid at 170°C for 6h. to give a brown oil, δ, 0.8-1.5 (m,3H), 1.8-2.8 (m,3H), 4.1-4.7 (broad s, 1H), 6.9-8.1 (m,14H). Unchanged spectrum when D_2O added; $\nu_{max.}$ 3300 (water), 3030, 2980 (broad), 2890, 1670(b), 1595, 1495, 1440, 1380, 1320, 1260, 1180 (broad), 1140, 1120, 1070, 1040, 950 and 900 cm^{-1}; $^{31}P(CDCl_3)$ = -37 (+ or - 4 p.p.m.) p.p.m.

Preparation of triphenylmethyl fluoroborate

Prepared using the method of Dauben [104] in good yield. Yellow crystals were obtained, m.p. 210-213°C after darkening.

Attempted preparation of 1,4-diphenyl-2-methyl-1,2-dihydrophosphinoline 1-oxide

1,4-Diphenyl-2-methyl-1,2-dihydrophosphinoline 1-oxide (2.4g, 7.2 mmols) was dissolved in acetonitrile (40 ml) and trityl fluoroborate (2.4g, 7.2 mmols) was added as an acetonitrile (30 ml) solution. The reaction mixture was then heated under reflux for 2h. After cooling, it was poured into water (250 ml) and extracted with dichloromethane

(3 ×25 ml). The organic fraction was dried over magnesium sulphate, filtered and removed under vacuum. Starting material was isolated in quantitative yield, identified by ^{1}H and ^{31}P n.m.r. spectra.

Preparation of 1-hydroxy-1,2,3,4-tetrahydrophosphinoline 1-oxide

Prepared using the method of Swan [99] et al. from 1-bromo-3-phenyl-propane in 44% yield (lit. [99] yield 46%), m.p. 146-147°C, (lit. m.p. [99] 146-147°C).

Preparation of 1-methyl-1,2,3,4-tetrahydrophosphinoline 1-oxide

1-Hydroxy-1,2,3,4-tetrahydrophosphinoline 1-oxide (3.0g, 16 mmols) was dissolved in toluene (dry, dist., 40 ml) and heated under reflux. Thionyl chloride (dist. 20 ml) was carefully added and the solution refluxed for a further 2½h. The solvent and excess thionyl chloride were removed by distillation and chased with benzene (50 ml). The residue was pumped under vacuum, to give crude 1-chloro-1,2,3,4-tetra-hydrophosphinoline 1-oxide. This was re-dissolved in benzene (50 ml) and added over 45 min. to methyl magnesium iodide (made from magnesium [0.5g, 20 mmols] and methyl iodide [3.12g, 22 mmols]) in ether (40 ml). The reaction mixture was refluxed for 2h. after the addition of the acid chloride, then cooled to 0°C. Ice (25g) and dilute hydrochloric acid (10% solution, 25 ml) were added, the product being extracted from the aqueous layer with chloroform, (3 × 50 ml). The combined organic fractions were dried over magnesium sulphate, filtered and the solvent removed under vacuum. 1-Methyl-1,2,3,4-tetrahydrophosphinoline 1-oxide was obtained as a crude product, orange crystals (2.8g, 94% yield). Purification was by column chromatography (U.G.1. alumina, 100g, eluted with ether increasing the polarity to 2% methanol/ether). The pure product was obtained as pale yellow crystals in 68% yield (m.p. 103-

106°C). An analysis sample was prepared by recrystallisation from dichloromethane/petrol (m.p. 107-109°C), $\nu_{max.}$ (nujol mull), 3060, 2950 (broad), 1950, 1850, 1650, 1600, 1575, 1490, 1450, 1420, 1305, 1290, 1270, 1170 (broad), 1085, 1050, 1035, 1015 and 930 cm^{-1}; δ, 1.8 (d,3H,J=15Hz), 1.9-2.7 (m,4H), 2.7-3.2 (m,2H), 7.1-8.2 (m,4H); m/e 180 (m^+), 178, 165, 147, 137, 117, 116, 115, 111, 109, 97, 95, 91, 89, 85, 83, 81 and 77; $C_{10}H_{13}PO$, Requires, C, 66.66; H, 7.22; P, 17.22; Found, C, 66.61; H, 7.41; P, 17.05; $^{31}P(CDCl_3)$ -28 p.p.m.

Preparation of 1-phenyl-1,2,3,4-tetrahydrophosphinoline 1-oxide

Prepared using Swan's [99,100] method in 74% yield (lit. yield 77%), b.p. 200°C at 0.015 mm Hg (lit. b.p. 180°C at 0.005 mm Hg), $\nu_{max.}$ (nujol mull) 2900 (broad), 1600, 1420, 1300, 1295, 1270, 1200, 1170, 1155, 1145, 1120, 1090, 1000, 920, 830, 790 and 730 cm^{-1}, m.p. 97-98°C (lit. m.p. 107-108°C); δ, 1.7-2.6 (m,4H), 2.8-3.2 (m,2H), 7.1-7.9 (m,9H); $^{31}P(CDCl_3)$ -25 p.p.m.

Preparation of 1-phenyl-1,2-dihydrophosphinoline 1-oxide

1-Phenyl-1,2,3,4-tetrahydrophosphinoline 1-oxide (1.2g, 5 mmols) was dissolved in carbon tetrachloride (50 ml) and the magnetically stirred solution was heated to reflux temperature. N-Bromosuccinimide (0.9g, 5 mmols) was added and the solution irradiated with a spot lamp for 35 min. The cooled solution was washed with dilute hydrochloric acid (100 ml, 2m) and water, then dried over anhydrous sodium sulphate. The pale brown oil crystallised on standing to give crude 4-bromo-1-phenyl-1,2,3,4-tetrahydrophosphinoline 1-oxide. Dehydrobromination was achieved with dimethylformamide (25 ml) heated at 110°C for 3h. The DMF was pumped off under vacuum, and the last traces removed with several portions of water. The residue was re-dissolved in dichloro-

methane, dried with magnesium sulphate, filtered and the solvent removed under reduced pressure.

1-Phenyl-1,2-dihydrophosphinoline 1-oxide (1g, 85% yield) was obtained as a pale yellow oil which solidified overnight. It was recrystallised from dichloromethane/cyclohexane to give white crystals, m.p. 98-101°C. The sample was purified for analysis by bulb to bulb distillation, b.p. 217-218°C at 0.027 mm Hg, m.p. 107-108°C; $\nu_{max.}$ (Film) 3400 (water), 3030, 2940, 2860, 1640, 1590, 1560, 1480, 1440, 1390, 1270, 1260, 1200 (broad), 1140, 1110, 1080, 1070, 1030, 1000, 930, 910, 860, 830, 820, 780 and 740 (broad) cm^{-1}, δ, 2.8-3.3 (m,2H), 5.7-6.8 (m,2H), and 7.2-8.1 (m,9H); m/e 241 (m+1), 240 (m^+), 191, 178, 165, 149, 134, 133, 125, 116, 115, 89 and 77; $C_{15}H_{13}OP$; Expect: C, 75.00; H, 5.42; P, 12.92; Found: C, 74.87; H, 5.68; P, 12.81; $^{31}P(CDCl_3)$ -21 p.p.m.

Preparation of 1-methyl-1,2-dihydrophosphinoline 1-oxide

1-Methyl-1,2,3,4-tetrahydrophosphinoline 1-oxide (0.9g, 5 mmols) was dissolved in carbon tetrachloride (50 ml), stirred magnetically and heated under reflux. N-Bromosuccinimide (1.1g, 6 mmols) was added and the solution irradiated with a spot lamp for 1h. The solution was cooled in ice, filtered and the solvent removed under reduced pressure. The crude bromide was dissolved in dimethylformamide (50 ml) then heated and stirred at 110°C for 45 min. The DMF was pumped off under vacuum and chased with several portions of water. The crude olefin was purified using column chromatography on alumina (UG1, 250g) eluted with chloroform. 1-Methyl-1,2-dihydrophosphinoline 1-oxide was obtained as a hydroscopic oil in 45% yield. An analysis sample was prepared by Kugelruhr distillation, 165-170°C at 0.04 mm Hg, followed by thick-layer chromatography (on silica plates eluted with methanol/chloroform, 1:5, R_t 0.6). The extract from the preparative plates was redistilled up a

sublimation tube and sealed under vacuum, b.p. 169-170°C at 0.04 mm Hg; $\nu_{max.}$ (neat) 3400 (water), 2940, 2890, 1720, 1670 (broad), 1600, 1450, 1420, 1310, 1180 (broad), 1140, 1090, 940 and 890 cm^{-1}, δ, 1.7 (d,3H,J=17Hz), 2.4-3.1 (m,2H), 5.7-6.8 (m,2H) and 7.1-8.2 (m,4H); m/e 179 (m+1), 178 (m^+), 163, 133, 117, 116, 115, 89 and 77; $C_{10}H_{11}PO$, Requires: C, 67.42; H, 6.18; P, 17.42; Found: C, 65.68; H, 6.35; P, 16.99; $^{31}P(CDCl_3)$ -28 p.p.m.

Preparation of 1-hydroxy-1,2-dihydrophosphinoline 1-oxide

Prepared following the procedure of Swan [99,100] in 57% yield from 4-bromo-1-hydroxy-1,2-dihydrophosphinoline 1-oxide, m.p. 155-156°C (lit. m.p. 156-157°C), sublimed 180°C at 0.1 mm Hg, δ, 2.9 (dd,2H,J=4 and 22Hz), 5.8-6.9 (m,2H), 7.2-8.3 (m,4H) and 9.9 (s,1H), m/e 180 (m^+), 162, 149, 134, 116, 115, 82, 81, 80 and 79, $^{31}P(CDCl_3)$ -36 p.p.m.

Preparation of 1-methoxy-1,2-dihydrophosphinoline 1-oxide

Prepared using the method of Swan [99,100] from 1-hydroxy-1,2-dihydrophosphinoline 1-oxide in 72% yield (lit. yield 85%). Separated from the unreacted acid by column chromatography (silica, MFC 25g) eluting with chloroform increasing the polarity to 1% methanol/chloroform, δ, 2.7 (dd,2H,J=5 and 20Hz), 3.6 (d,3H,J=14Hz), 5.7-6.8 (m,2H), 7.2-8.3 (m,4H); $^{31}P(CDCl_3)$ -35 p.p.m. One peak by g.l.c. (10% SE30, 210°C, N_2 = 12 psi, H_2 = 17 psi, air = 14 psi, 0.4 µl, 2 min/cm) retention time = 6.2 min.

Preparation of 4-methyl-1-phenyl-1,2-dihydrophosphinoline 1-oxide

4-Methyl-1-phenyl-1,2,3,4-tetrahydrophosphinoline 1-oxide (3.0g, 12 mmols) was dissolved in carbon tetrachloride (300 ml) and N-bromosuccinimide (2.1g, 12 mmols) was added to the refluxing solution. The reaction mixture was irradiated with a spot lamp for 1h., then cooled,

the solvent was removed under reduced pressure and the residual oil left overnight. The crude product (4.8g) was purified by column chromatography on silica (Keselgell, 170g, packed in ether) and eluted with ether increasing the polarity to 5% methanol/ether. 4-Methyl-1-phenyl-1,2-dihydrophosphinoline 1-oxide (2.4g) was obtained in 81% yield. An analysis sample was prepared by distillation, 173-174°C at 0.1 mm Hg, to give a hydroscopic oil; $\nu_{max.}$ (CH_2Cl_2 solution), 3300 (water), 3030, 3000, 2960, 2890, 1600, 1480, 1450, 1290, 1220, 1190, 1125, 1080, 1060, 1040, 820 and 790 cm^{-1}, δ, ($CDCl_3$/TMS), 100 MHz, 2.08 (dd,3H,J=2 and 4Hz), 2.0-3.3 (m,2H), 5.84 (dt,1H, J=25 and 6Hz), 7.25-7.95 (m,9H), m/e 256 (m+2), 255 (m+1), 254 (m^+), 253, 252, 227, 224, 192, 191, 175, 165, 133, 130, 129, 128, 125, 115, 91 and 77; ε_{312nm}= 522, ε_{238nm}= 407; $C_{16}H_{15}PO$; Expect: C, 75.59; H, 5.91; P, 12.20; Found: C, 73.62; H, 6.35; P, 11.80; these figures give good argument for a 3% water content. $^{31}P(CDCl_3/TMS)$ -24 p.p.m.

General Procedure for photolysis reactions

All irradiations were carried out in a Rayonet photochemical reactor, the samples were contained in quartz tubes (25 ml capacity) fitted with rubber septums. All solutions were degassed with dry nitrogen and photolysed with ultra-violet light (λ = 254 nm). The reactions were followed by gas chromatography and/or ^{31}P n.m.r. spectroscopy.

Dark reaction of 4-methyl-1-phenyl-1,2-dihydrophosphinoline 1-oxide in methanol

4-Methyl-1-phenyl-1,2-dihydrophosphinoline 1-oxide (105 mg, 0.4 mmols) was dissolved in degassed methanol and the solution degassed for a further 30 min. The quartz tube was left in the dark at room tempera-

ture for one week. The solvent was removed under reduced pressure and the residual oil (99 mg, 0.39 mmols) was identified as unchanged starting material by n.m.r. spectroscopy (94% recovery).

Photolysis reaction of 4-methyl-1-phenyl-1,2-dihydrophosphinoline 1-oxide in methanol

4-Methyl-1-phenyl-1,2-dihydrophosphinoline 1-oxide (700 mg, 2.7 mmols) was dissolved in methanol (150 ml, degassed) and degassed for a further 30 min. The solution was irradiated with u.v. light ($\lambda = 254$ nm) until all the starting material had reacted. The reaction was followed by gas chromatography (sampled at $1\frac{1}{2}$, 3, $4\frac{1}{2}$ and 6h.) the retention times (3% OV 17 column; $N_2 = 10$ psi, air = 16 psi, $H_2 = 14$ psi, temp. = 290°C, chart speed 10 cm/min; sample size 0.1 µl) for the photolysis products were 13.8, 15, 16.8, 39.6 and 43.2 sec. The starting olefin had a retention time of 37.2 sec. Thin layer chromatography (silica, eluted with ether) gave R_f values of 0.01, 0.19 (major product), 0.27 and 0.77, the original olefin had a value of 0.06. A gas chromatography/mass spectrum of this photolysis mixture showed the products to be three isomers of methyl phenyl-2-(2^1-butenyl)-phenyl-phosphinate. The products with longer retention times were adducts between these isomers and unreacted starting material. See Table 1. The ^{31}P n.m.r. spectrum showed peaks at -33.4 (14%), -32.8 (61%), -31 (12%) and -22 (13%) p.p.m.

Separation of Photolysis products from the reaction mixture

The crude photolysis products were placed on a silica column (Kesel-gel, 25g, packed and eluted in ether) to separate them from the unreacted starting material. The separation of one isomer from another proved very difficult, as shown by g.l.c. of column fractions, even

after repeated chromatography. Preparative gas chromatography did separate out the isomers but only in low yields. A pure sample of methyl phenyl-2-(trans-2^1-but-2-enyl)-phenylphosphinate *(237)* was obtained by a combination of the above techniques. The yields of the various products were *(237)* 55%, minor photolysis products *(236)* 25% and starting material 20%, although these yields were dependent upon concentration of the solution and irradiation times. Sufficient amounts of the minor products could not be isolated.

Methyl phenyl-2-(trans-2^1-but-2-enyl)-phenylphosphinate

$\nu_{max.}$ (CH_2Cl_2 solution); 3060, 2950 (broad), 2860, 2350, 1595, 1560, 1480, 1440, 1220, 1140, 1130, 1120, 1040, 840 and 790; δ, 100 MHz; 1.44 (dd,6H,J=2 and 6Hz), 3.7 (d,3H,J=12Hz), 4.9-5.1 (m,1H), 7.0-8.0 (m,9H), m/e 287 (m+1), 286 (m^+), 272, 271, 257, 255, 253, 243, 239, 225, 221, 199, 195, 192, 191, 165, 163, 156, 155, 149, 141, 131, 130, 129, 128, 116, 115, 91 and 77; b.p. 0.02 mm Hg, 149-150°C; $C_{17}H_{19}PO_2$, Requires: C, 71.33; H, 6.64; Found: C, 70.19; H, 6.88, sample contains small amount of water. Purified for analysis by thick layer chromatography followed by distillation and sealing under vacuum, a difficult sample to handle; g.l.c. 1 peak conditions as in Table 1, R_t = 27 min., ^{31}P n.m.r. ($CDCl_3$/TMS) -33 p.p.m.

Attempted use of other trapping agents in the photolysis of 4-methyl-1-phenyl-1,2-dihydrophosphinoline 1-oxide. Hydrogenation of crude photolysis mixture.

4-Methyl-1-phenyl-1,2-dihydrophosphinoline 1-oxide (350 mg, 0.14 mmols) was dissolved in methanol (100 ml) and photolysed with u.v. light (λ = 254 nm) for 3h. The solvent was removed under reduced pressure and an n.m.r. spectrum recorded. The sample was re-dissolved in methanol (30 ml) and placed in a hydrogenater with palladium upon charcoal (10%,

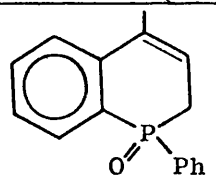
1 spatula) for 5h. The solution was filtered twice through filter aid and the methanol removed under vacuum. The residue (221 mg) was found to contain less olefinic protons. This oil was re-dissolved in methanol (30 ml) and replaced in the hydrogenater with some palladium upon charcoal (10%, 1 spatula) for a further 25h., 0.166g, 47% recovery. Thin layer chromatography showed the presence of a new product. Separation by thick layer chromatography gave 4-methyl-1-phenyl-1,2,3,4-tetrahydrophosphinoline 1-oxide *(224b)* both isomers, band one. The second band was a mixture of the unhydrogenated photolysis products (all three isomers) and two minor products $^{31}P(CDCl_3)$ -44 p.p.m. Gas chromatography (3% OV 17 230°C, $N_2 = 8$ psi; $H_2 = 15$ psi; sample 0.2 µl; chart speed 2 min/cm) showed the only identifiable product to be *(224b)*. Retention times of the photolysis products were 12.6, 13.8, 14.4, 23 and 56 min., the products of the reaction had retention times of 8.8, 9.9 and 13 (broad) min. 4-Methyl-1-phenyl-1,2,3,4-tetrahydrophosphinoline 1-oxide had a retention time of 8.8 min.

Attempted photolysis in acetonitrile with tetrachloroethylene

4-Methyl-1-phenyl-1,2-dihydrophosphinoline 1-oxide (215 mg, 0.85 mmols) was dissolved in tetrachloroethylene (distilled at 120-121°C, and degassed for 30 min.), and the solution irradiated for 2h. The solvent was removed to give the starting olefin only. The sample was re-dissolved in acetonitrile (dry and degassed) with tetrachloroethylene (296 mg, 1.8 mmols, an excess) then photolysed ($\lambda = 254$ nm) for 3h. The solvent was removed under reduced pressure to give a complex mixture which contained a large number of phosphorus containing compounds [$^{31}P(CDCl_3)$, -19, -27, -28, -32, -38 and -45 p.p.m.] It was not possible to separate out a single product by thick-layer chromatography (on silica).

TABLE 1

GC/MS of the u.v. irradiations ($\lambda = 254$ nm) in methanol of



G.l.c. conditions were: 3% OV 17 column, Temp. 115°C, Sample size 2 µl, Chart speed 10 cm/min., N_2 0.2.

Retention times (minutes)	Mass Spectra m/e	Assignments
25	287, 286, 285, 272, 271, 258, 256 255, 254, 243, 239, 225, 221, 209 195, 192, 191, 178, 165, 163, 156 155, 141, 131, 130, 129, 128, 116 115, 91, 79, 78, 77.	
27 (Major Product)	287, 286, 285, 273, 272, 271, 258 257, 255, 253, 244, 243, 241, 239 225, 221, 209, 199, 196, 195, 193 192, 178, 165, 163, 156, 155, 149 141, 133, 131, 130, 129, 128, 127 116, 115, 91, 89, 79, 78, 77	*(237)*
30	287, 286, 285, 272, 271, 258, 256 254, 243, 239, 225, 221, 209, 192 191, 178, 165, 163, 156, 155, 141 131, 130, 129, 128, 116, 115, 91 78, 77.	
44 } 46	543, 542, 541, 529, 528, 527, 526 467, 466, 465, 464, 452, 457, 409 394, 390, 376, 375, 374, 316, 315 257, 255, 253, 243, 197, 195, 187 179, 165, 156, 91, 78, 77.	

Metastable peak 386 (526 → 451)

$^{31}P = -22$
Adducts of the above isomers and starting material.

Attempted photolysis in acetonitrile with dimethyl acetylene-dicarboxylate

4-Methyl-1-phenyl-1,2-dihydrophosphinoline 1-oxide (258 mg, 1 mmol) was dissolved in acetonitrile (degassed for 30 min.) and dimethyl acetylenedicarboxylate (856 mg, 6 mmols, excess freshly distilled) was added. The solution was photolysed for 2h. (λ = 254 nm) then the solvent was removed under reduced pressure. The resulting residue was placed on an alumina column (UG1, packed in ether) eluted with ethyl acetate increasing the polarity to 5% methanol/ethyl acetate then methanol. The only identifiable product was starting material. A polymeric product (n.m.r. $H^1(CDCl_3)$, δ, 3.6-4.0 (m), 7.1-8.0 (m)), was also obtained. ^{31}P n.m.r. showed the major product at -22 p.p.m. Thick layer chromatography failed to isolate this compound, it was presumably too polar.

Attempted photolysis in acetonitrile

4-Methyl-1-phenyl-1,2-dihydrophosphinoline 1-oxide (85 mg, 0.3 mmols) was dissolved in acetonitrile (30 ml) and the solution degassed for 40 min. It was then photolysed (λ = 254 nm) for 2h. The solvent was removed under vacuum. A reaction appeared to have taken place but no products were isolated. ^1H n.m.r. ($CDCl_3$), δ, 1.0-2.4 (m,6H), 5.2 (m,1H), 7.1-8.0 (m,9H).

Photolysis in t-butanol

4-Methyl-1-phenyl-1,2-dihydrophosphinoline 1-oxide (154 mg, 0.6 mmols) was dissolved in t-butanol (dry, distilled, degassed, 25 ml) and the solution degassed (30 min.) before irradiation for 2h. (λ = 254 nm). The solvent was removed under reduced pressure, starting material was found to be present. The residue was redissolved in t-butanol (25 ml),

degassed and photolysed for a further 3h. Gas chromatography (3% OV 17, 270°C, N_2 = 10 psi, H_2 = 15 psi, air = 15 psi, sample 0.1 µl, chart 2 min/cm) showed the presence of 5 new peaks (9, 11.6, 12.4, 14.8 and 16.8 min.), the starting material had a retention time of 26 min.

Photolysis in t-butylamine

4-Methyl-1-phenyl-1,2-dihydrophosphinoline 1-oxide (125 mg, 0.5 mmols) was dissolved in t-butylamine (purified by refluxing over potassium hydroxide and distillation, 25 ml, degassed for 30 min.) and the solution degassed for 40 min. It was photolysed (λ = 254 nm) the reaction being followed by gas chromatography (3% OV 17, 300°C, 1 cm/min., sample 0.3 µl, N_2 = 10 psi, air = 10 psi, H_2 = 15 psi), samples being taken at 1, 2, $2\frac{1}{2}$ and 3h. The starting olefin had a retention time of $5\frac{1}{2}$ min. After 1h. two new peaks appeared in the GLC, with retention times of 2.2 and 2.3 min. (60:40). All the starting material had been converted into these two new products after 3h. Purification was by column chromatography (Keselgel silica, 7.5g) packed and eluted with ethyl acetate, then 50/50 ethyl acetate, methanol, and distillation, 140°C at 0.9 mm Hg. N-t-butyl-phenyl-2-(2^1-but-2-enyl)-phenylphosphine-amide was obtained as a pure clear oil in 34% yield, δ, 100 MHz; 1.3 (d,9H,J=12Hz), 1.6-3.0 (m,5H), 4.8-5.6 (m,2H), 5.7-6.5 (m,1H) and 7.2-8.2 (m,9H); m/e 328 (m+1), 327 (m^+), 313, 312, 272, 271, 270, 257, 256, 255, 254, 253, 239, 236, 221, 194, 192, 191, 189, 180, 163, 149, 148, 140, 130, 129, 128, 121, 111, 110, 92 and 91; $C_{20}H_{26}NOP$ requires C, 73.39; H, 7.95; N, 4.28; Found: C, 72.15; H, 8.00; N, 4.63; Re-run found: C, 70.65; H, 7.82 and N, 4.36. Difficult to handle, therefore not possible to obtain phosphorus analysis; $^{31}P(CDCl_3/TMS)$ -24 p.p.m.

Photolysis reactions of 1-methyl-1,2-dihydrophosphinoline 1-oxide

1-Methyl-1,2-dihydrophosphinoline 1-oxide (439 mg, 2.5 mmols) was dissolved in methanol (degassed, 70 ml) and the solution degassed for 30 min. It was photolysed with u.v. light (λ = 254 nm), the reaction being monitored by gas chromatography. After 1½h. all the starting material had reacted to give predominately one compound (75%) and minor products. The retention time of starting olefin (10% SE 30, 200°C, sample 0.2 µl; N_2 = 12 psi, H_2 = 15 psi, air = 15 psi, 2 cm/min.) was 7.8 min. The products had retention times of 4.2 (75%), 4.9 (13%), 5.8 (6%) and 6.6 (6%) min. Purification of these fractions was by thick layer chromatography (silica, 12% methanol/chloroform, R_f, major fraction 0.66) and separation by preparative gas chromatography (10% SE 30, 200°C, N_2 = 60 psi, air = 50 psi, H_2 = 17 psi, N_2 and air 25 kg/cm^2, outlet heater 250°C, trap heater, high; heaters A & B = 3; sample size 50 µl, trap cooled in 40% water/60% ethylene glycol/dry ice at -10°C) to give the major product, identified as methyl methyl-2(prop-3^1-enyl)-phenylphosphinate, a clear oil, δ, 100 MHz, 1.7 (d,3H,J=16Hz), 3.7 (d,5H,J=12Hz), (the two benzyl protons appear under the P-OMe doublet), 4.9-5.2 (m,2H), 5.8-6.2 (m,1H), 7.2-7.6 (m,3H), 7.8-8.0 (m,1H); m/e 211 (m+1), 210 (m$^+$), 208, 195, 194, 182, 181, 180, 179, 178, 177, 169, 167, 165, 164, 149, 117, 116, 115, 94, 93, 91, 89, 79 and 77; ^{31}P($CDCl_3$/TMS) -44 p.p.m. Gas chromatography separated two isomers of this product. Both were shown to have ^{31}P($CDCl_3$/TMS) values of -44 p.p.m., and mass spectral parent ions at 210. These minor products could not however be isolated in sufficient yield for analysis.

Attempts to prepare 4-methoxy-1-methyl-1,2-dihydrophosphinoline 1-oxide

1-Methyl-1,2,3,4-tetrahydrophosphinoline 1-oxide (134 mg, 0.75 mmols) was dissolved in tetrachloromethane (30 ml) and heated to reflux

temperature under nitrogen. N-Bromosuccinimide (134 mg, 0.75 mmols) was added and the solution irradiated for 30 min. The solvent was removed under vacuum to give crude, 4-bromo-1-methyl-1,2-dihydrophosphinoline 1-oxide as a yellow oil. The product was dissolved in methanol and filtered into another flask, sodium methoxide in methanol (prepared by taking $^{1}/_{10}$th. of a solution containing sodium) (170 mg, 7.5 mmols) in methanol (7 ml) was then added. After stirring at room temperature for 20 min. the solution was refluxed for 1h. The colour of the reaction mixture changed from yellow to brown during this time. Water (50 ml) was added to remove the excess methoxide and the product extracted with ether. 1-Methyl-1,2-dihydrophosphinoline 1-oxide was obtained (35 mg 26% recovery). The ^{31}P spectrum also showed a peak at -24.6 p.p.m. (6%).

From 1-methyl-1,2-dihydrophosphinoline 1-oxide

Mercuric acetate (150 mg, 0.47 mmols, recrystallised from acetic acid and dried in a drying pistol overnight) and methanol (15 ml) were placed in a flask. 1-Methyl-1,2-dihydrophosphinoline 1-oxide (84 mg, 0.47 mmols) in methanol (10 ml) was then added to the vigorously stirred solution. After 10 min. the mercurial intermediate was reduced with sodium hydroxide (3M, 10 ml) and sodium borohydride (0.5M, 10 ml) both as water solutions. The mixture turned deep yellow upon addition of sodium hydroxide and grey when the sodium borohydride was added. The solution was stirred for 2h. and the mercury allowed to settle at the bottom of the flask. After decanting, the methanol solution was filtered through filter aid (celite), twice, and the bulk of the solvent removed. The product was obtained by extraction with dichloromethane to give unreacted 1-methyl-1,2-dihydrophosphinoline 1-oxide (46 mg) in 55% recovery, n.m.r., ^{31}P n.m.r. The reaction was repeated

stirring for 48h. before the reduction step. Only starting material was obtained (t.l.c. silica R_f 0.57, methanol/chloroform 1:8).

Photolysis reactions of 1-phenyl-1,2-dihydrophosphinoline 1-oxide

1-Phenyl-1,2-dihydrophosphinoline 1-oxide (143 mg, 0.6 mmols) was dissolved in methanol (25 ml, degassed) and the solution degassed for 40 min. It was then photolysed with u.v. light (λ = 254 nm), the progress of the reaction being followed by gas chromatography (10% SE 30, 210°C, N_2 = 12 psi, H_2 = 12 psi, air = 15 psi, sample size 0.2 µl, 5 min/cm), samples taken every 30 min. After 1½h. the solvent was removed, however starting material still present (by ^1H and ^{31}P n.m.r.). The sample was redissolved in methanol and degassed as before. Photolysis for a further 1½h. and removal of solvent under reduced pressure gave the products with all the starting olefin reacted (by ^1H, ^{31}P n.m.r. and G.L.C.). The retention times of the products were 17 (major product), 19 and 40 to 55 (broad peak) min. 1-Phenyl-1,2-dihydrophosphinoline 1-oxide had a retention time of 36 min. (broad peak) under these conditions. The photolysis products were separated by thick layer chromatography twice (silica plates) and eluted with methanol/chloroform in the ratio 1:8. The products had R_f values of 0.7 (major product), 0.51 and 0.27, they were obtained in 61% overall yield. Each fraction was shown to be isomeric by its ^{31}P n.m.r. and mass spectrum. Methyl phenyl-2-(prop-2^1-enyl)-phenylphosphinate was identified as the major product. The $^{31}P(CDCl_3)$ n.m.r. spectrum after 1½h. was -37 (6%), -36 (10%), -33.8 (37%), -33.2 (14%) and -21.7 (33%) p.p.m., after a further 1½h. this had changed to -34.6 (66%), -34 (22%) and -27 (12%) p.p.m. 1-Phenyl-1,2-dihydrophosphinoline 1-oxide had a $^{31}P(CDCl_3)$ n.m.r. of -21 p.p.m.

Methyl phenyl-2-(prop-2^1-enyl)-phenylphosphinate, contained a small

amount of the minor isomeric products. $\nu_{max.}$ (CH_2Cl_2 solution); 3020, 2960, 2920, 2830, 1640, 1595, 1470, 1440, 1380, 1270, 1220, 1180, 1140, 1120, 1035, 1025, 1000, 920 and 800 cm^{-1}, b.p. 119-120°C at 0.5 mm Hg, δ, 1.3-1.9 (m, methyl groups of the cis and trans isomers of the prop-1^1-enyl product), 3.8 (s,2H), 3.9 (d,3H,J=12Hz), 4.8-5.2 (m,2H), 5.6-6.4 (m,1H), 7.2-7.8 (m,7H) and 7.8-8.3 (m,2H); m/e 273 (m+1), 272 (m^+), 271, 258, 257, 241, 240, 239, 225, 195, 192, 191, 181, 178, 165, 163, 157, 156, 155, 149, 141, 133, 117, 116, 115, 91, 89, 79, 78 and 77. Analysis for $C_{16}H_{17}PO_2$ requires: C, 70.59; H, 6.30; P, 11.40; Found: C, 69.22; H, 6.28; P ----- and C, 69.44; H, 6.43; P -----; $^{31}P(CDCl_3)$ -33 p.p.m.

Photolysis reactions of 1-methoxy-1,2-dihydrophosphinoline 1-oxide

1-Methoxy-1,2-dihydrophosphinoline 1-oxide (176 mg, 0.9 mmols) was dissolved in methanol (degassed) and the solution degassed for 20 min. Photolysis with u.v. light (λ = 254 nm) for 1h. gave only starting material by gas chromatography (10% SE 30, 210°C, N_2 = 12 psi, H_2 = 17 psi, air = 14 psi, sample size 0.4 μl, chart speed 2 min/cm) of a sample from the photolysis mixture. After 3h. irradiation products appeared, after 4h. only 50% of the starting material remained and after 5h. only 40%. All the original olefin had reacted after 26h., and one product was obtained (165 mg) in 80% yield (93% recovery). By GLC three peaks are observed, they have retention times of 3.4 (4%), 3.8 (82%) and 5.0 (14%) min. Distillation, 100-101°C at 0.025 mm Hg gave dimethyl 2-(prop-2^1-enyl)-phenylphosphonate as a clear oil. $\nu_{max.}$ (CCl_4 solution) 3080, 3000, 2960, 2850, 1640, 1600, 1570, 1470 (broad), 1255, 1190, 1140, 1080, 1060, 1035, 920 and 835 cm^{-1}, δ, 3.9 (d,8H,J=12Hz), the two benzyl protons appearing under the P-OMe doublet, 5.0-5.4 (m,2H), 5.8-6.5 (m,1H), 7.4-7.6 (m,3H) and 7.8-8.3 (m,1H); m/e 227 (m+1), 226

(m^+), 225, 212, 211, 198, 193, 182, 179, 163, 162, 117, 116, 115, 91 and 89, $^{31}P(CDCl_3/TMS)$ -22 p.p.m.

EXPERIMENTAL CHAPTER FOUR

Preparation of Diethylphosphorochloridite

This compound was prepared using the method of Saunders [125] from one mole equivalent of phosphorus trichloride to two mole equivalents of triethyl phosphite. Diethylphosphorochloridite was obtained in 41% yield, b.p. 760 mm, 140-143°C, ^{31}P n.m.r. -165 p.p.m. (lit. b.p. 760 mm Hg, 143-148°C, ^{31}P n.m.r. -165 p.p.m., 50% yield), δ, 1.4 (t,6H,J=8Hz), 4.2 (m,4H,J=8Hz).

Preparation of methyl phosphorodichloridite

Prepared using the method of Martin [126] in 32% yield, b.p. 89-90°C, ^{31}P n.m.r. -180 p.p.m. (lit. [127] b.p. at 758 mm Hg = 95-96°C; ^{31}P n.m.r. -180.5 p.p.m., 60% yield).

Preparation of 2-ethoxy-5-methyl-1,2-oxaphospho1-3-ene 2-oxide

Diethylphosphorochloridite (18.2g, 0.14 mmols) was placed in a three necked flask (100 ml) under nitrogen at 0°C. Methyl vinyl ketone (distilled) (9.6g, 0.14 mmols) was then added over 10 min. The reaction mixture was allowed to warm up to room temperature then stirred under nitrogen for two days to give 2,2-diethoxy-2-chloro-5-methyl-1,2-oxaphospho1-3-ene. This was heated at 100°C for 14h., until ethyl chloride was no longer evolved, to give 2-ethoxy-5-methyl-1,2-oxaphospho1-3-ene (13.4g, 60% yield), b.p. at 1.5 mm Hg = 90-92°C. ^{31}P n.m.r. -48 p.p.m., δ, 1.5 (t,3H,J=8Hz), 1.8 (s,3H), 2.4 (dm,2H,J=14Hz and 2Hz), 4.2 (quintet 2H,J=8Hz and 2Hz) and 5.0 (dm,1H,J=32Hz), $\nu_{max.}$ (neat) 3090, 2950, 2930, 1720, 1675, 1480, 1450, 1430, 1410, 1385, 1280, 1270, 1230, 1160, 1100, 1040, 970, 910, 830 and m/e 163 (m+1), 162 (m^+), 161, 138, 137, 135, 134, 133, 111, 110, 109, 99, 97, 91, 83, 82 and 81.

Preparation of 2-chloro-5-methyl-1,2-oxaphosphol-3-ene 2-oxide

Prepared using the method of Novitskii [128] from methyl phosphorodichloridite and methyl vinyl ketone in 28% yield as a clear oil, b.p. 1.5 mm Hg 100-105°C; ^{31}P n.m.r. = -59 p.p.m., δ, 2.0 (m,3H), 3.0 (m,2H) and 5.3 (d,1H,J=40Hz), m/e 155, 154, 153, 152, 117, 116, 71 and 70 (lit. yield 39%, b.p. at 0.5 mm Hg, 73°C).

Preparation of 2-ethoxy-4,5-benzo-1,2-oxaphosphol-3-ene 2-oxide

The compound was prepared from triethyl phosphite and o-(hydroxymethyl) phenol using the method of Ageeva [129] in 80%, b.p. 0.03 mm Hg 120-123°C, (lit. yield 82%, m.p. 59-60°C, b.p. 122°C at 0.03 mm Hg), ^{31}P n.m.r. -28 p.p.m.

Reactions of 2-ethoxy-5-methyl-1,2-oxaphosphol-3-ene 2-oxide

The apparatus was flame dried under dry nitrogen before each experiment.

A. Reaction with sodium methoxide in methanol

2-Ethoxy-5-methyl-1,2-oxaphosphol-3-ene 2-oxide (509 mg, 0.0031 moles) was dissolved in methanol (dried and distilled, 20 ml) and sodium methoxide (1 mole equivalent) in methanol was added. ^{31}P n.m.r. spectrum -26 p.p.m. (87%), -27 (13%), δ, 1.0-2.0 (m), 3.0-4.2 (m), 3.3 (d,J=10Hz). The product would not distil and was not soluble in dichloromethane. Addition of methanol caused solidification.

B. Reactions with non-nucleophilic bases

i. Lithium diisopropylamide

1. Diisopropylamine (0.09 cm^3, 6.2×10^{-4} moles) (freshly distilled after refluxing over KOH 1h., 83-84°C) in tetrahydrofuran (15 ml, freshly distilled from $LiAlH_4$, 64-65°C), was placed in a 3-necked round bottom flask. Methyl lithium in ether (1.5 cm^3, 0.42 molar) was injected

through a rubber septum to the solution, and cooled to -78°C; a white precipitate formed. 2-Ethoxy-5-methyl-1,2-oxaphosphol-3-ene 2-oxide (112 mgs, 6.9×10^{-4} moles) in tetrahydrofuran (20 cm^3) was then added.

After a few min. deuteromethanol (0.025 cm^3, 1 mole equivalent) was added and the solution allowed to warm up to room temperature. The solvent was removed under reduced pressure, δ, 1.6-2.4 (m) and 3.5-4.4 (m).

2. Lithium diisopropylamide prepared from diisopropylamine (0.94 cm^3) and n-butyl lithium (3.9 cm^3 as a 1.7M in hexane solution) in tetrahydrofuran (15 ml) was left to stir at -78°C for 15 min. 2-Ethoxy-5-methyl-1,2-oxaphosphol-3-ene 2-oxide (1.09g, 0.0067 moles) in tetrahydrofuran (5 ml) warmed to -10°C was then added; the solution turned green. After stirring for a further 20 min. it was recooled to -78°C and benzaldehyde (0.68 cm^3, 0.006 moles) was added. After 15 min. the green colour changed to a brown colour. The solution was allowed to warm up to room temperature. Hydrochloric acid (2N) was poured into the flask following an overnight stir, the product was extracted with CH_2Cl_2 then dried over $MgSO_4$, the t.l.c. showed benzaldehyde still to be present. The solvent was removed to give a brown oil (1.4g); ^{31}P n.m.r. ($CDCl_3$) -43.6 p.p.m., 10.7%; -33 p.p.m., 24.2%; -31 p.p.m., 22.2%; -27 p.p.m., 31.8%; -21 p.p.m., 11.1%; δ, 1.0-1.6 (m), 1.8-3.8 (m), 3.8-4.6 (m), 6.8-8.4 (m) and 11.0 (broad s).

ii. Butyl Lithium

2-Ethoxy-5-methyl-1,2-oxaphosphol-3-ene 2-oxide (0.914g, 5.6×10^{-5} moles) was dissolved in THF (15 ml) and stirred at -78°C; t-butyl lithium (2.8 cm^3, 5.6×10^{-3} moles) was injected through a septum into the flask. A dark green colour developed which was still present after the addition of benzaldehyde (0.6g, 5.6×10^{-3} moles). After stirring

overnight the solution was brown in colour. It was poured into water (100 ml) and the product extracted with ether (3 × 50 ml), dried over magnesium sulphate, filtered and the solvent removed under reduced pressure. A number of products (114.4 mg, 12.5%) were obtained. Column chromatography (silica, 30g, packed and eluted in ether increasing polarity to 5% methanol in stages) gave benzaldehyde and the four other unidentified peaks, δ, 0.18-1.6 (m,11H), 2.2-2.5 (m,1H), 3.4-4.4 (m,4H), 7.2-8.0 (m,10H) and 10 (s,1H).

iii. Hexamethyldisilazane

1. Hexamethyldisilazane (1.42 ml, 6.8 mmols) was added to THF (15 ml) in a round bottom flask (100 ml) and cooled to -78°C; n-butyl lithium (4 ml, 1.6 molar) was injected into the flask, which was then allowed to warm up to room temperature for 10 min. It was recooled to -78°C and 2-ethoxy-5-methyl-1,2-oxaphosphol-3-ene 2-oxide (1.09g, 6.7 molar) in THF (10 ml) added. The solution was allowed to warm up to -10°C for 1h. After cooling to -78°C, benzaldehyde (0.71g, 6.8 mmols) was injected into the flask and the solution allowed yet again to warm up to room temperature. Hydrochloric acid (2N) was added and the product extracted with chloroform. An attempt to separate out the products by column chromatography (50g UG1 alumina, packed and eluted with 60-80°C petrol increasing polarity to ethyl acetate then methanol). The fractions were dried over magnesium sulphate. No product could be identified from the n.m.r.

2. Hexamethyldisilazane (1.6 ml, 7.9 mmols) was placed in a round bottom flask (100 ml) with THF (25 ml). The solution was cooled to -78°C; n-butyl lithium (6.5 ml, 1.2 molar, 7.9 mmols) was then injected through a septum and it was allowed to warm back to room temperature for 10 min. After recooling to -78°C 2-ethoxy-5-methyl-1,2-oxaphosphol-

3-ene 2-oxide was added. After the addition the solution was stirred at -10°C for 40 min., then methyl iodide (1.1g, 7.7 mmols) was added. The reaction mixture was stirred at room temperature for 30 min. before removal of the solvent. An attempt to distil the product (up to 200°C, 0.1 mm Hg) failed. The salt, probably $(CH_3)_3Si\text{-}\overset{+}{N}(CH_3)_2Si(CH_3)_3,I^-$ was dissolved in water and the product extracted with CH_2Cl_2. ^{31}P n.m.r. gave peaks at -73 p.p.m. (22.6%), -70 p.p.m. (13.3%), -31 p.p.m. (43.9%) and δ, 0.8-1.8 (m), 1.8-2.4 (m), 3.8-4.5 (m), 5.6 (d,J=20Hz), and 11.0 (broad s).

Reactions of 2-chloro-5-methyl-1,2-oxaphospho1-3-ene 2-oxide

i. With lithium diisopropylamide

1. Diisopropylamine (0.99 ml, 7 mmols) was dissolved in THF (15 ml) and stirred at -78°C; n-butyl lithium (4.2 ml of 1.7M solution) was injected into the flask. 2-Chloro-5-methyl-1,2-oxaphospho1-3-ene 2-oxide (1.08g, 7 mmols) was added after 15 min. The solution was stirred for a further 10 min. before deuteromethanol (MeOD, 0.28 ml, 7.0 mmols) was added. The solution was allowed to warm up to room temperature, the product extracted with CH_2Cl_2 and ether. Dimethyl-1^1-(butan-3-one)-phosphonate was the white crystalline product obtained.

2. (a) Diisopropylamine (0.81 ml, 5.8 mmols) in THF (15 ml) was placed in a flask with n-butyl lithium (3.4 ml, 5.8 mmols) and the mixture stirred at -78°C. the chloride (295) (0.9g, 5.8 mmols) was added. After stirring at -10°C then recooling to -78°C, dimethyl acetylenedicarboxylate (0.71 ml, 5.8 mmols) was then added and the solution allowed to warm up to room temperature. The solvent was removed under vacuum to give the dimethyl ester of diisopropylamino-maleic acid (1.6g). Recrystallised twice from CH_2Cl_2 m.p. 118-119°C, δ, 1.3 (d,12H,J=10Hz), 3.8 (d,J=20Hz), 3.5-4.0 (m,6H) and 4.8 (s,1H).

(b) Dimethyl acetylenedicarboxylate (0.88 ml, 7 mmols) and diiso-

propylamine (1 ml, 7 mmols) were mixed together in THF (15 ml). The solution exothermed and turned to a brown colour. After removal of the THF under vacuum the dimethyl ester of diisopropylaminomaleic acid was obtained (1.9g, 53% yield). Recrystallisation with CH_2Cl_2 four times, gave a m.p. at 118-119°C, δ, 1.3 (d,12H,J=10Hz), 3.8 (d,J=20Hz), 3.5-4.0 (m,6H) and 4.8 (s,1H).

ii. Reaction with hexamethyldisilazane

Hexamethyldisilazane (1.1 ml, 5.4 mmols) in THF (15 ml) was stirred at -78°C. n-Butyl lithium (3.4 ml, 1.6 molar) was added and the solution was stirred at room temperature for 1h. After recooling to -78°C, 2-chloro-5-methyl-1,2-oxaphosphol-3-ene 2-oxide (0.8g, 5.4 mmols) was added. Following stirring at -10°C for 1½h. and cooling back to -78°C, deuteromethanol (MeOD, 0.5 ml, 5.4 mmols) was added to the reaction mixture. The solution was warmed to room temperature, a white precipitate formed, the solvent was removed under vacuum and the residue taken up in HCl (2N). The product was then extracted with CH_2Cl_2. ^{31}P n.m.r. -34 p.p.m., δ, 0.6-3.0 (m), 3.4-4.2 (m), 3.6 (d,J=10Hz).

The vacuum flash thermolysis of 2-chloro-5-methyl-1,2-oxaphosphol-3-ene 2-oxide

At 400°C

The thermolysis apparatus was the same as used in Chapter 3. Deuteromethanol (CH_3OD) was placed in the U-tube and cooled solid in liquid nitrogen. The apparatus was then evacuated down to 0.025 mm Hg. Opening of the stopcock and warming up of the U-tube causing deuteromethanol to be deposited upon the 'cold finger'. 2-Chloro-5-methyl-1,2-oxaphosphol-3-ene 2-oxide (294 mg, 2 mmols) was placed in a 5 ml flask at the end of the apparatus. The furnace was then heated to 400°C and

the oven slowly heated to 100°C. After the passing of the sample through the hot spot and condensing it on the 'cold finger', a further layer of deuteromethanol was added to the 'cold finger sandwich'. The apparatus was allowed to cool to room temperature before the methanol was passed through the furnace.

Warming of the 'cold finger' to room temperature and collecting the products into a 5 ml flask under nitrogen, followed by removal of the excess deuteromethanol gave 84 mg (29% yield) of crude reaction product, white crystals, ^{31}P n.m.r. -34 p.p.m., δ, 1.8-2.4 (m), 3.8 (d,J=6Hz and 9.6Hz).

ii. At 700°C

The apparatus was set up as for previous experiment, however dimethyl acetylenedicarboxylate was used instead of deuteromethanol as the trapping reagent. The apparatus was evacuated to 0.015 mm Hg, then 2-chloro-5-methyl-1,2-oxaphosphol-3-ene 2-oxide (0.55g, 3.6 mmols) was thermolysed at 700°C, the oven temperature was slowly increased to 120°C. A second layer of dimethyl acetylenedicarboxylate was 'sandwiched' on top of the thermolysis products, the whole apparatus was allowed to warm up to room temperature before the products were washed from the 'cold finger' with deuterochloroform. Only dimethyl acetylenedicarboxylate and the 2-chloro-5-methyl-1,2-oxaphosphol-3-ene 2-oxide were identified as products. ^{31}P n.m.r. -59 p.p.m.

iii. At 900°C

The above experiment was repeated, with the furnace at 900°C, an excess of dimethyl acetylenedicarboxylate and 2-chloro-5-methyl-1,2-oxaphosphol-3-ene (0.7g, 4.6 mmols). The product obtained had a ^{31}P n.m.r. -48 p.p.m.

Thermolysis of N-phenylaziridine

N-Phenylaziridine (100 mg, 0.8 mmols) was heated at 200°C for 18h. in a flask under nitrogen, δ, 2.1 (s, 37%), 3.4 (s, 63%); N-phenylaziridine, δ, 2.1 (s). A sample of N-phenylaziridine in ethanol was converted to polymer at 180°C for 3h., 3.4 (s), all the ethanol was distilled off.

Attempted trapping reaction

N-Phenylaziridine (100 mg, 0.8 mmols) was heated in refluxing indene (182°C, 1 ml) for 3h. Unchanged starting material was obtained as a product.

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