TRANSFORMATIONS OF CYCLIC PHOSPHORUS IMINES

by

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Thesis presented for the degree

of

DOCTOR OF PHILOSOPHY

University of Edinburgh 1979

CONTENTS

DECLARATION

I declare that this thesis is my own composition, that the work of which it is a record has been carried out by myself, and that it has not been submitted in any previous application for a Higher Degree.

The thesis describes the results of research carried out in the Department of Chemistry, University of Edinburgh, under the supervision of Professor J.I.G. Cadogan, since the 1st October 1973, the date of my admission as a research student.

ACKNOWLEDGEMENTS

I should like to thank Professor J.I.G. Cadogan for suggesting the research topic and for his advice and encouragement throughout the course of the work.

In addition I should like to thank my colleagues in the laboratory for their help and advice on many occasions, and in particular, Mr. J. Millar for teaching me to use the Varian HA-100 N.M.R., Dr. A. Boyd for his help in running the phosphorus spectra on the XL-100 Fourier Transform N.M.R., and Mr. T. Naisby in his capacity as laboratory technician. I should also like to thank Mrs. Manson for her excellent typing of this thesis.

Finally, I thank the Science Research Council for the award of a Maintenance Grant during my period in the laboratory.

POSTGRADUATE LECTURES

I attended the following lectures and conference to obtain the required number of eight units for postgraduate study.

1) Attendance for 3 years at Laboratory 10 group seminars. 3 units

2) Attendance at a series of five lectures by Professor R. Sugden and colleagues of Shell Petroleum on "Oil Related Products Research". 1 unit

3) Attendance at a series of five lectures by Dr. A. Bellamy, University of Edinburgh, on "Recent Advances in the Theory of Concerted Processes". 1 unit

4) Attendance at a series of five lectures by Dr. R.K. Harris, Varian Associates, on "N.M.R. Spectroscopy". 1 unit

5) Attendance at a series of five lectures by Professor J.I.G. Cadogan and Dr. I. Gosney, University of Edinburgh, on "Organophosphorus Reagents in General Organic Synthesis". 1 unit

6) Attendance at a week long course at the University of Keele, sponsored by the Science Research Council and the Careers Research Advisory Council, on "The Various Aspects of Commercial Management". 1 unit

TO MY PARENTS

FOR THEIR SUPPORT AND ENCOURAGEMENT

THROUGHOUT MY UNIVERSITY CAREER

ABSTRACT

The concepts of "pseudorotation" and "turnstile rotation" in phosphorane species are discussed in the light of the literature evidence available. This leads to the concepts of "apicophilicity" and "apicophobia" of various ligands in such species.

Results of various kinetic experiments are then discussed in view of these concepts and the theory that ring strain plays a major part in the rates of reactions involving phosphoranes as intermediates or transition species is developed with emphasis on the accelerations noted in rate when smaller rings are present.

This theory is then postulated as explanation of the observed decompositions of various phospholimines by Cadogan and Scott [1, 2] and the zero reaction of various acyclic phosphinimines. To test this theory a variety of cyclic and acyclic phosphinimines were synthesised and allowed to decompose at 160° in bromobenzene while the reaction was followed by ^{1}H N.m.r. spectroscopy. Various rates of reaction were observed dependent on ring size and the apicophilicity of the atoms bonded to phosphorus.

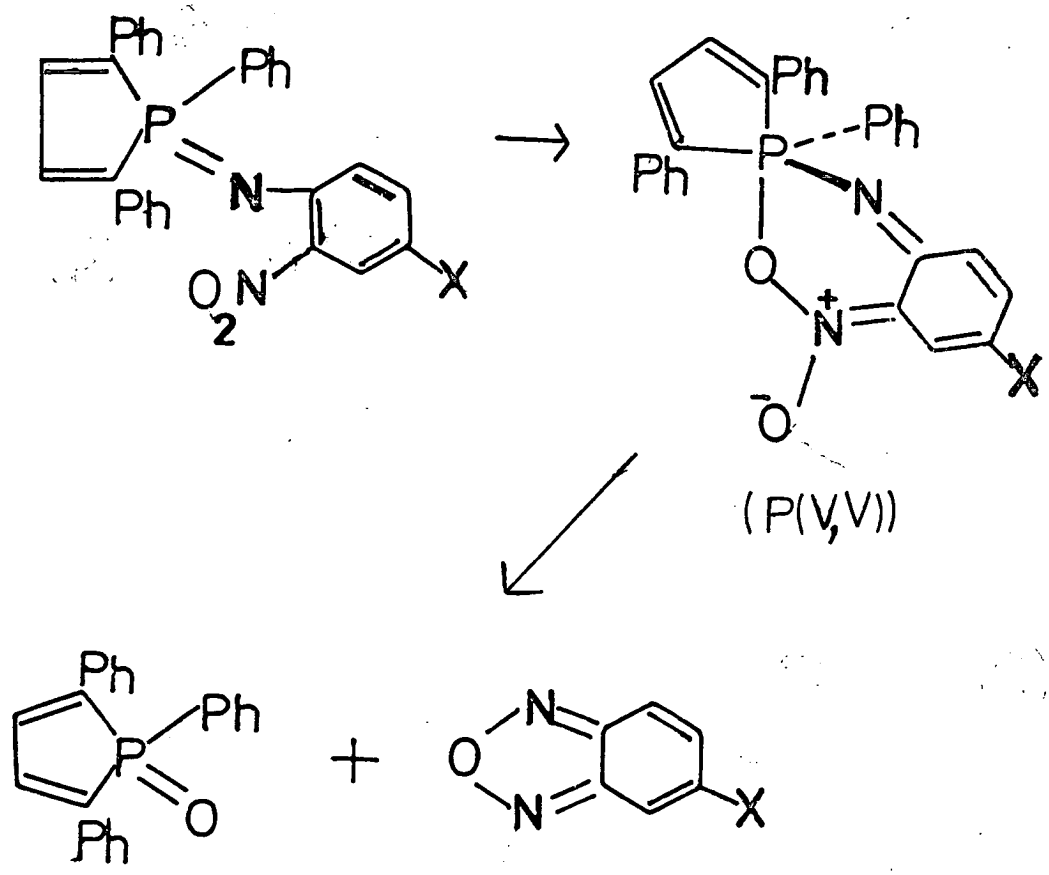
A notable result was the very slow rate of reaction, comparatively, when the phosphorus was constrained in a dioxaphospholan type ring. This result led to observations of the reaction by ^{31}P N.m.r. and an intermediate species was noted in this reaction. No such intermediate was noted when the phosphorus was constrained in a phosphole or phospholan type ring.

A further major result was the observation of the formation of 4-substituted-3-nitroanilines in these reactions which was shown to occur even during vacuum thermolysis so excluding hydrolysis as the cause. These observations led to a revision of the reaction mechanism as proposed by Cadogan and Scott.[1, 2]

INTRODUCTION

Preamble

Cadogan, Gee and Scott[1,2] have shown that 1-N-o-nitroarylimino-1,2,5-triphenylphospholes undergo thermolysis at 150-160° to give 1,2,5-triphenylphosphole oxide and the corresponding substituted benzofurazans (Scheme 1).



SCHEME 1

Evidence from competitive deoxygenation reactions[2] has indicated this to be an intramolecular reaction proceeding via attack, of the oxygen atom of the neighbouring nitro-group, on the phosphorus atom,

to give a bicyclic pentaco-ordinate intermediate or transition species.

As the corresponding triethyl N-o-nitrophenylphosphorimidate ($(EtO)_3P=NAr$) and triphenyl-N-o-nitrophenylphosphinimine ($Ph_3P=NAr$) do not undergo this decomposition, while N-o-nitrophenylphosphoramidic trichloride ($Cl_3P=NAr$) gave the benzofurazan it was at first thought that the phospholimine ylide function ($\equiv\overset{+}{P}-\overset{-}{N}-$) was relatively more polarised than in the P-triphenyl and P-triethoxy derivatives.[1] However, attempts to extend this reaction to other phosphorus moieties soon led to anomalous results, and it became clear that polarisation differences could not entirely account for the variations in reactivity.

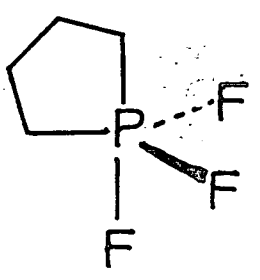
It is known[3] that ring strain can be relieved on forming a pentaco-ordinate trigonal bipyramidal type of transition species (in SN2 reactions at carbon). This suggested that the driving force for the decomposition of the 1-N-o-nitrophenyl-1,2,5-triphenylphospholes was relief of such strain in the phosphole ring on formation of the five valent, pentaco-ordinate phosphorane designated (P(V,V)) in Scheme 1.

It was therefore decided to synthesise a variety of cyclic phosphorus imines in an attempt to demonstrate that reactivity differed with ring size. This thesis describes the result of this study, and it will therefore be of value to consider, in the following discussion, the factors involved in the stability of pentacovalent, pentaco-ordinate phosphorus species, and the effects this stability has on the reactivity of the molecules involved with comparison between acyclic species and analogues of various ring size.

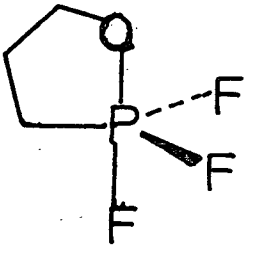
Pentaco-ordinate Pentacovalent Phosphorus Species - Phosphoranes

Ring Strain: (a) Five-membered Rings

Ugi et al[4] have shown, from molecular orbital calculations of binding energies in phosphoranes, that the ring envelope can accommodate an angle of 90° at phosphorus with almost no strain, while an angle of 120° created a good deal of strain. This confirmed the experimental observations of Muetterties and Schmutzler,[5] who found that the ring in (1) could be placed apical/equatorial with an angle of 90° at phosphorus, and by Ugi himself,[4] of the apical/equatorial ring in (2), even though this contradicts the polarity rule (see "Apicophilicity" p.17) which would predict that the apical positions should be occupied by fluorine atoms with the ring diequatorial.



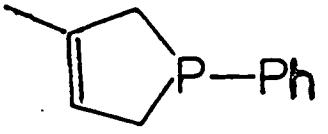
(1)



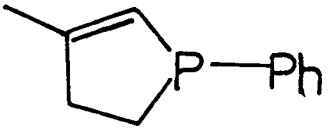
(2)

Westheimer[6] has also shown that apical/equatorial placement is energetically more favourable than the diequatorial, while Kenyon[7] found that the kinetics of ^{18}O exchange in a series of acyclic, monocyclic and bicyclic phosphine oxides indicated that there is no great energy difference between a tetrahedral four co-ordinate phosphorus species and phosphoranes with the ring diequatorial. However it is known that under certain circumstances the ring

can be placed diequatorially. Denney[8] has found evidence for this in the reaction of the phospholenes (3) and (4) with diethyl peroxide giving isoprene and diethyl phenylphosphonite, which undoubtedly

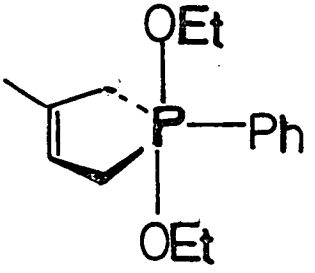


(3)



(4)

proceeds via phosphoranes of the type (5) and (6) where (6) interconverts to (5) by ionisation and tautomeric hydrogen shift. The phosphorane (5) then gives the products by a reverse cycloaddition.



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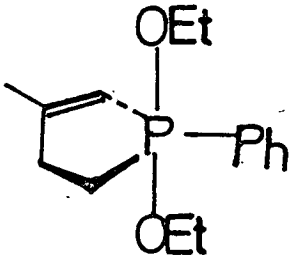
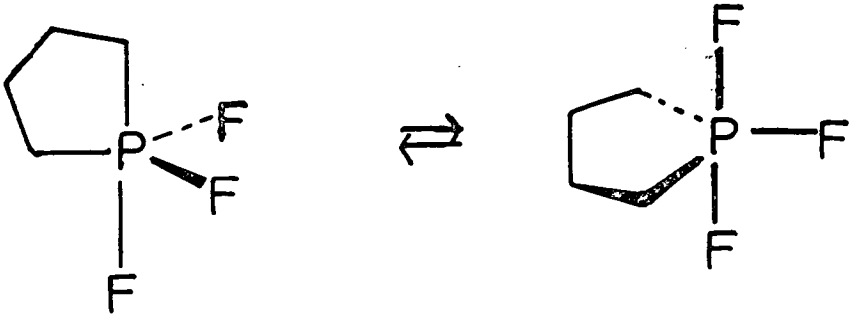


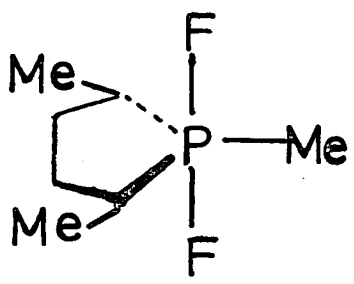
(6)

Muetterties[5] observed a rapid exchange of equatorial and apical fluorine atoms in (1), which was explained as a rapid equilibrium of the type shown in Scheme 2, while De'Ath and Denney[9] have



SCHEME 2

observed that at low temperatures the diequatorial form is the sole species in (1), as is the case in (7), though (8) has a mixture of diequatorial and apical/equatorial in the ratio 1:2.3. Kenyon[7] found that the ring in (9) went diequatorial during his ^{18}O exchange studies.



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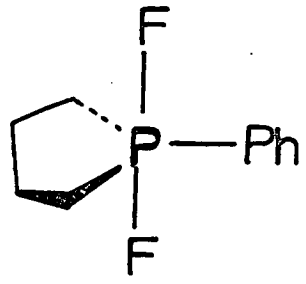

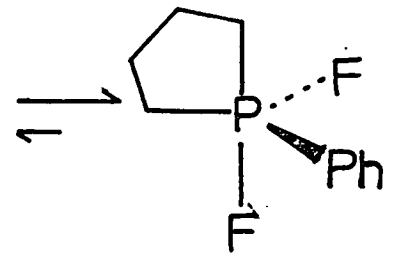

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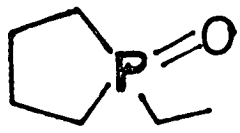

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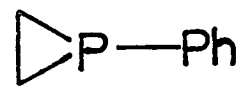
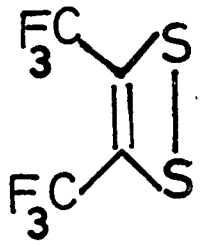


(10)

(b) Three and Four-membered Rings

Literature on the thermally unstable three-membered cyclic phosphorus compounds, or phosphirans is scanty. Denney[10] has shown, however, that 1-phenylphosphiran (10) failed to give a phosphorane with diethyl peroxide and trifluoromethyl hypofluorite. This failure suggests that if the reaction were to proceed in similar fashion to that mentioned previously for (3) and (4) the phosphiran refuses to be placed diequatorially. Certainly,

placing the ring in such a configuration would require a good deal of energy input in comparison to a four-membered ring, which equilibrates apical/equatorial, diequatorial rapidly on the N.M.R. time scale at 30°.[11] When (10) was reacted with the dithietene (11) at -78°,[10] the trivalent compound (12) was obtained. As De'Ath and Denney[12] had previously shown that (11) gave phosphoranes with trivalent phosphorus compounds, the formation of (13) as an intermediate seems reasonable.



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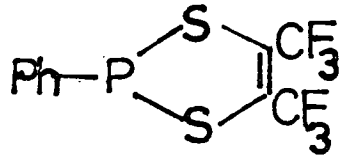

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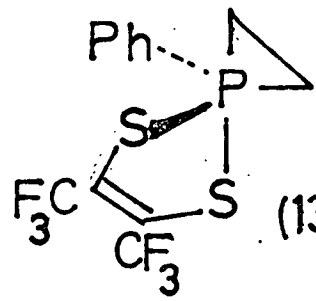
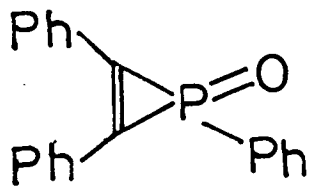


(13)

1,2,3-Triphenylphosphirene oxide (14) has been allowed to react with sodium hydroxide, and was found to give the ring opened product, 1,2-diphenylvinylphenylphosphinic acid (15), which, at 120°, itself collapses to 1,2-diphenylethylene.[13] It would appear reasonable to suppose attack of hydroxide on (14) should



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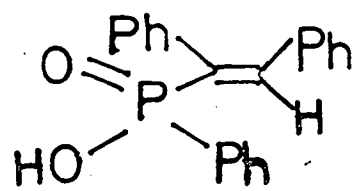


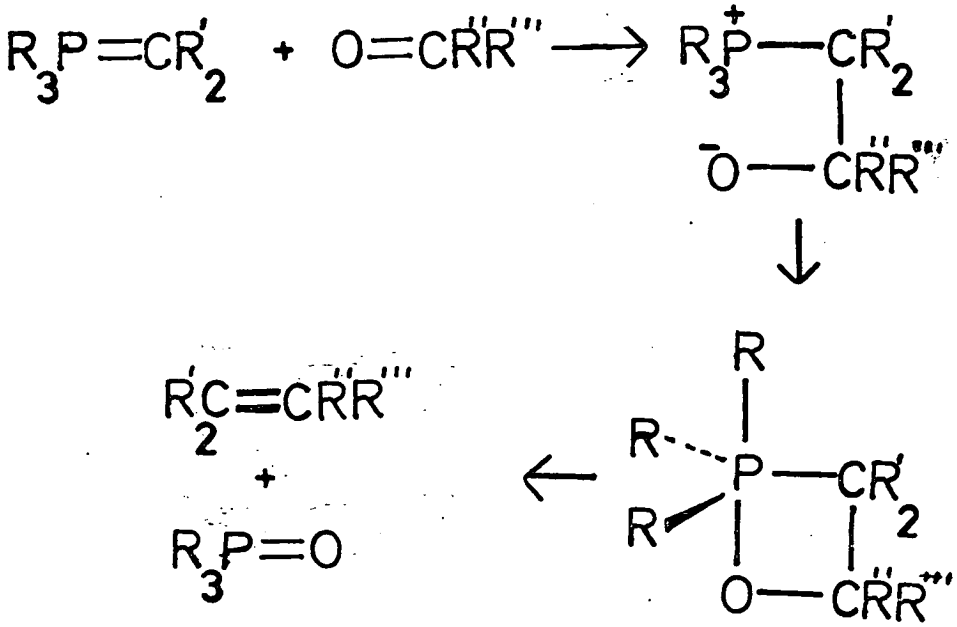
(15)

give only the <u>cis</u> ring opened product as collapse of the vinyl carbanion formed should be rapid compared to rotation to give the <u>trans</u> isomer, and indeed the product was found to be 3:1 <u>cis</u>:<u>trans</u>

isomer as expected. The oxide was also found to decompose, to 1,2-diphenylacetylene, only at 120° under low pressure, which tends to confirm the findings of Vilceneau[14] that there is a barrier to the spontaneous decyclisation of phosphirans, not as a result of the conservation of orbital symmetry but due to the high deformation of bond angles, and hence the increase in strain, in the hypothetical transition states.

These results seem to suggest, therefore, that while the formation of phosphoranes containing the phosphiran ring is possible, they will tend to decompose rapidly; that the ring will be placed exclusively apical/equatorial, and that ring opening will tend to play a major part in any reaction involving nucleophilic attack at phosphorus.

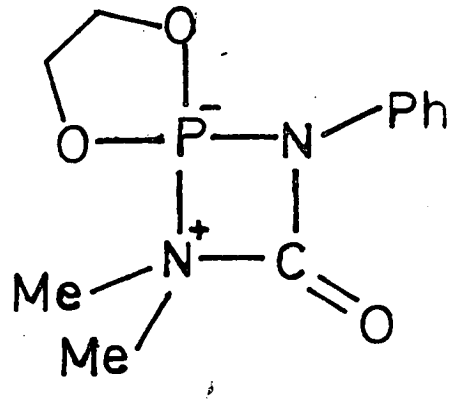
Four-membered ring phosphetans on the other hand, form phosphoranes with comparative ease, and pentavalent phosphorus constrained in a four-membered ring has been postulated in several applications of the Wittig reaction as shown in Scheme 3.[15,16]



SCHEME 3

This postulate is endorsed by the observations of Aksnes and Khalil[17] of appreciable solvent effects on Wittig reactions. In particular they noted that the transition state in solvents of low polarity was less polar than the reactants, suggestive of a four-membered transition species.

In a similar reaction, Hudson[18] has proposed a four-membered transition state in the reaction of phosphoramidates with aldehydes and ketones. Further, in agreement with the expected acceleration due to the formation of a cyclic, stabilising bicyclic intermediate with relief of ring strain the reaction of 2-N-dimethyl-1,3,2-dioxaphospholan with benzaldehyde is about 1150 times faster than the acyclic analogues. Acceleration is also noted in the reaction with isocyanates when the transition state would be (16)



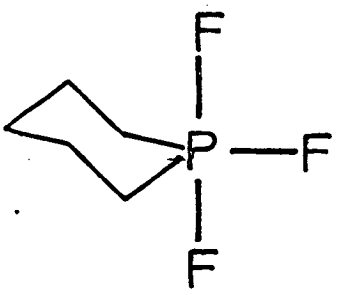
(16)

Denney et al[11] have shown for carbocyclic phosphetan rings that at low temperatures the ring remains apical/equatorial, while above 30°, as previously mentioned, the ring can be placed diequatorially. However, the four-membered ring definitely displays a preference for the apical/equatorial placement as Trippett[19] has shown that the adduct of 1-phenyl-2,2,3,4,4-pentamethyl-phosphetan and hexafluoroacetone, even at 160°, shows no tendency to place

the ring diequatorially. Ramirez[20] has shown that the four-membered ring is less strained when apical/equatorial than when diequatorial, and indeed has noted[4] that pentavalent oxaphosphetans are locked in the apical/equatorial position, with the ring oxygen atom apical.

(c) Six-membered Rings

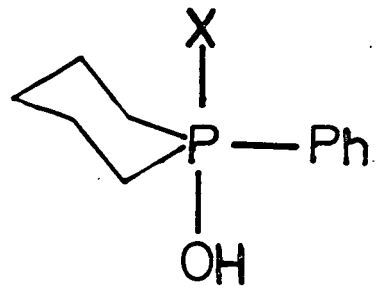
Ugi[4] has shown that the six-membered ring containing trifluorophosphorane (17) has non-equivalent fluorine atoms, such that the ring must be locked in the diequatorial position.



(17)

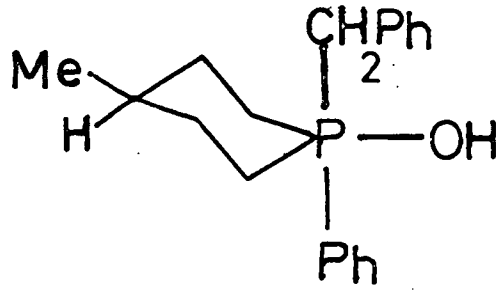
Ramirez[20] has stated that, other element considerations so allowing (see "Apicophilicity" p.17), six-membered rings prefer the diequatorial placement, as they are free of the strain constraints to which smaller rings are subject, but that they can also be placed apical/equatorial.

Further evidence for the diequatorial placement of the ring has come from the observation that displacement reactions at phosphorus in six-membered rings normally occurs with inversion of configuration, as in acyclic systems, suggesting an intermediate phosphorane of type (18), where displacement takes place along the apical axis faster than any possible ligand isomerisation (see "Pseudorotation" p.11).



(18)

Marsi and Clark,[21] however, have noted an apparent exception, where, in the hydrolysis of 1-phenyl-1-benzyl-4-methylphosphorinanium salts, while inversion was preferred, some retention of configuration did occur. This has been interpreted[20] in terms of an intermediate species of type (18), with X = $-CH_2Ph$, which has undergone ligand reorganization to (19), before loss of benzyl anion, so giving retention.



(19)

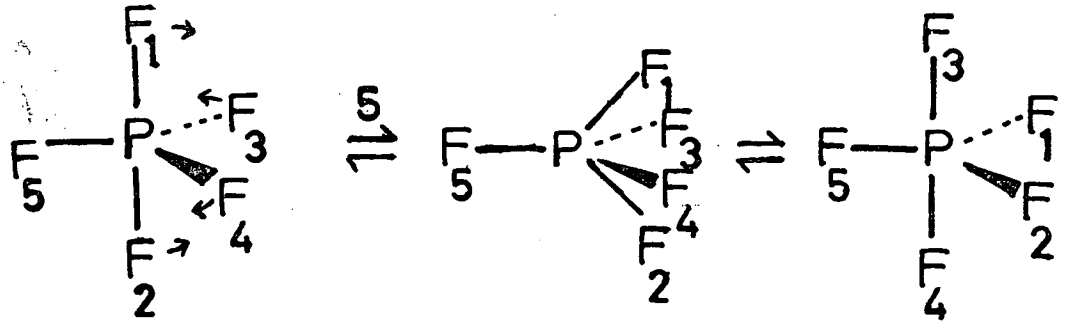
(d) Seven- and Eight-membered Rings

Marsi[22,23] has shown that seven-membered rings experienced complete inversion of configuration during hydroxide cleavage of their benzyl salts, and that the analogous eight-membered phosphorane derivative reacted with preponderant, if not complete, inversion. Following the arguments for six-membered rings, above, this suggests that rings larger than six-membered are placed diequatorially in phosphorane species and, in the absence of ring strain, behave analogously with their acyclic analogues.

Pseudo-rotation and Turnstile Rotation

While square pyramidal rather than trigonal bipyramidal geometry has occasionally been found for stable phosphoranes,[24] or pentaco-ordinated intermediates or transition states,[25] the great bulk of X-ray structure determinations on cyclic phosphoranes has indeed shown the latter geometry, with four- and five-membered rings in the apical/equatorial position.[20]

In trigonal bipyramids it is known that the apical bonds are longer and weaker than the equatorial bonds.[6] The ^{19}F spectrum of PF_5 would therefore be expected to give two lines, but only one line is actually observed.[26] Berry[27] proposed the concept of "pseudo-rotation" to explain this ligand equivalence where using one equatorial fluorine as a "pivot" and interchanging the other four in two pairs via, effectively, a square pyramidal intermediate as shown in Scheme 4, the ligands become equivalent by using each fluorine as "pivot" in turn.

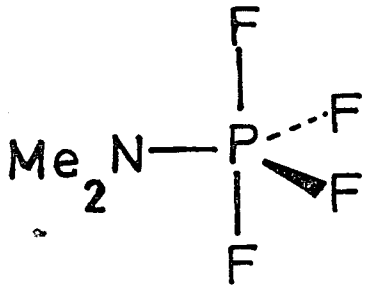


SCHEME 4

(atom no. given at the equilibrium sign is that of the atom used as pivot in the isomerisation).

With rings, as mentioned in the previous section, able to take up different positions on the trigonal bipyramidal skeleton it has been noted[4,5] that such ligand isomerisation can also occur in cyclic phosphoranes, the isomerisation occurring either by a "regular" type of process only involving bond deformations or by an "irregular" process involving bond cleavage and formation,[4] proceeding via a tetra- or hexaco-ordinate species.

Muetterties[28] has described several types of possible processes of the "regular" type. Whitesides and Mitchell[29] have observed, however, that the fluorine atoms in N-dimethyltetrafluorophosphorane (20) interchange by a process involving "inseparable couples" of fluorine atoms.



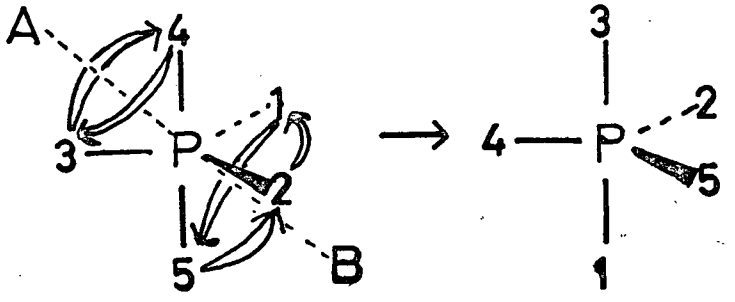
(20)

This observation precludes all but one of the processes considered by Muetterties, this being the "pseudo-rotation" process described in Scheme 4.

Ugi et al[4] have since shown, however, that there is a process not considered by Muetterties which is also consistent with the Whitesides-Mitchell experiment.

This process, which has been termed "turnstile rotation", involves pairing an apical and an equatorial ligand, and coupling the remaining three as a trio. The pair and the trio, then rotate, in turnstile rotation, in opposite directions about a

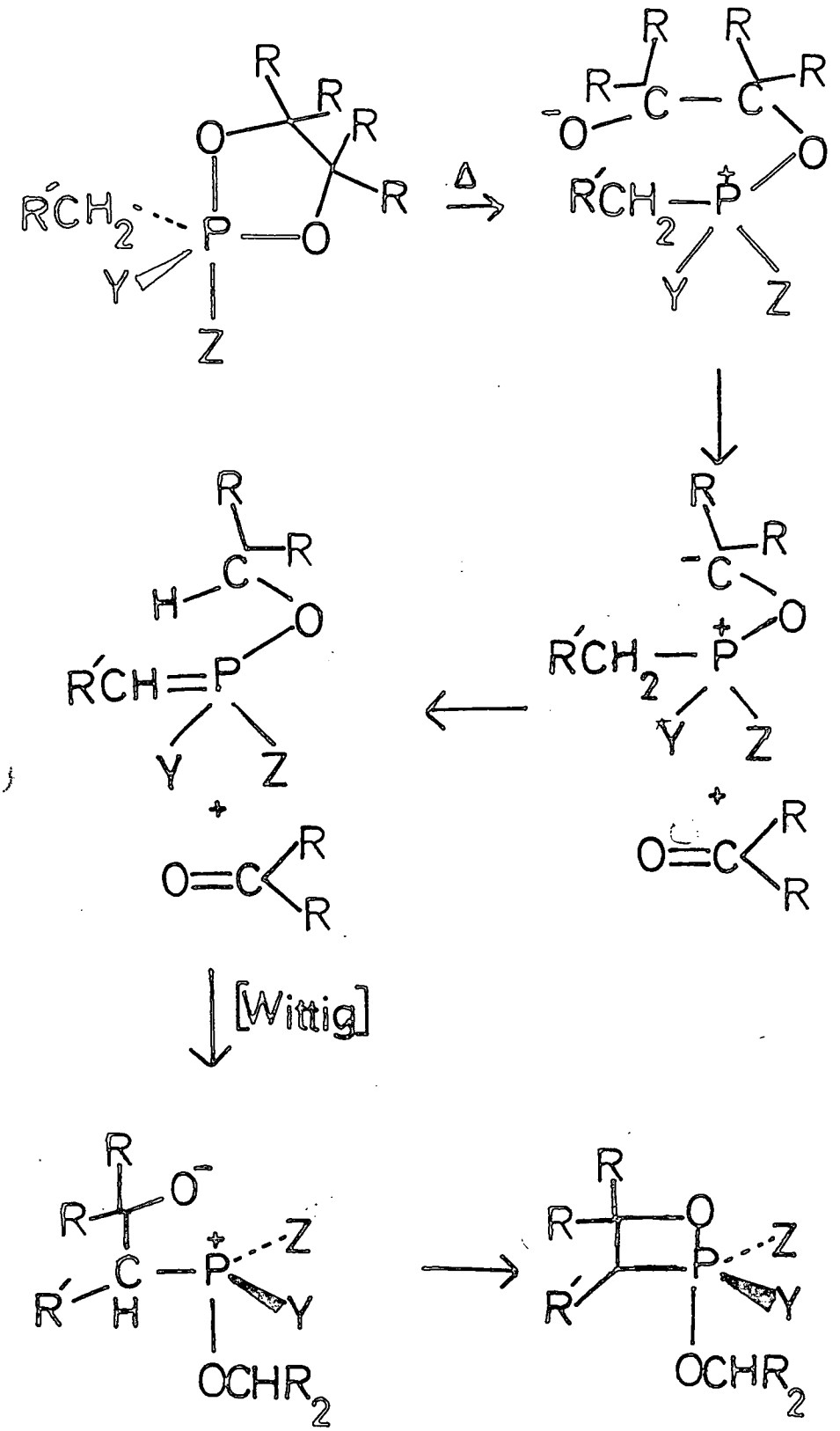
line which lies in the plane of the two apical ligands and one equatorial ligand, and bisects the solid angle between the other two equatorial ligands and an apical ligand, such as the line AB in (21).



(21) (22)

Rotation of the pair and trio in opposite directions leads to (22), the pair having rotated through 180° and the trio through 120°. While ligand 2 is still equatorial, apical ligands 4 and 5 are now equatorial and equatorial ligands 1 and 3 are now apical. Continuation of the process about AB and similar axes will result in ligand equivalence.

From the foregoing discussion it can be seen therefore that both processes are regular rearrangements of trigonal bipyramidal pentaco-ordinate species yielding equivalent products. Both processes are energetically allowed and both exchange apical and equatorial ligands pairwise in a concerted, synchronous manner. In the ideal case both processes can proceed with conservation of angular momentum. The processes differ however in the partitioning of the ligand set, pseudo-rotation being (1+4), turnstile rotation (2+3), all ligands participating in a turnstile rotation. It can be shown[4] that there are four turnstile rotations producing the same net result as any pseudo-rotation, when it would seem that turnstile rotation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Y
OCHR2

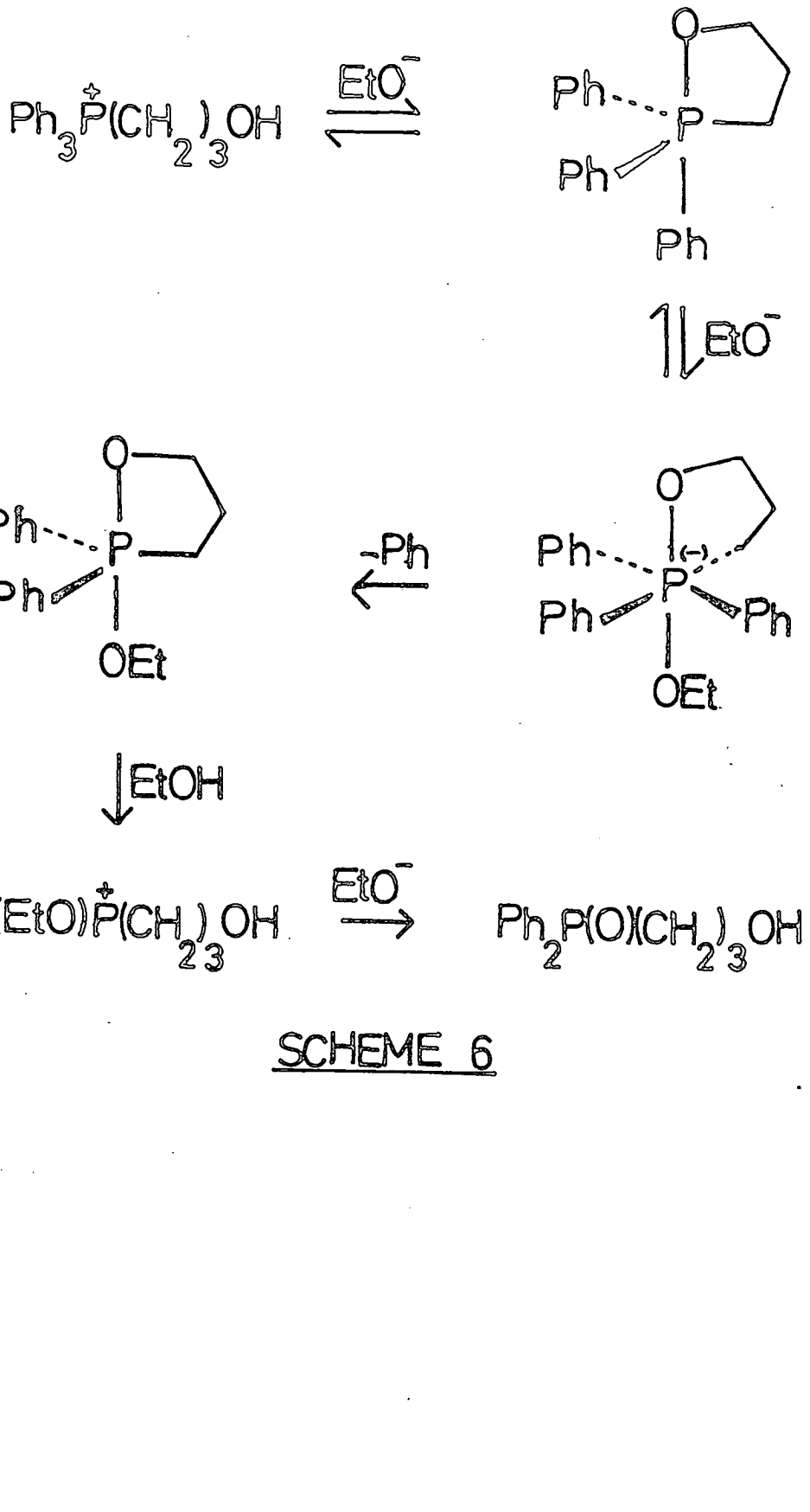
SCHEME 5

would have a higher probability than a pseudo-rotation process although quantum mechanical calculations[30,31] have shown that the turnstile rotation process would be expected to demand slightly more energy than a pseudo-rotation. Furthermore the motions leading to the barrier species in each process are different,[4] multiple turnstile rotations being possible without passing through a trigonal bipyramidal intermediate, an ability not shared by pseudo-rotation, and the ligand motions and energy barriers vary differently as a function of the ligand set and its distribution on the trigonal bipyramidal skeleton. Ugi et al[4] have, indeed, concluded that trigonal bipyramidal species with apical/equatorial rings must rearrange by turnstile rotation.

Finally, a major difference is the fact that turnstile rotation is essentially an internal rotation while rotation is entirely absent in the Berry process, this merely being a bond reorganisation, and in fact, the term pseudo-rotation can be misleading.

While the two processes described above are normally responsible for ligand isomerisation, irregular processes have been observed. - An example of this type of rearrangement is the formation of 1,2-oxaphosphetans from 1,3-oxaphospholans on pyrolysis, as shown in Scheme 5.[32]

Ramirez[20] has noted other examples while Asknes[33] has suggested a mechanism for the alkoxide promoted decomposition of 3-hydroxypropyltriphenylphosphonium chloride involving ethoxide ion attack on a pre-equilibrated pentacovalent intermediate to give a hexaco-ordinate species which has sufficient energy to split off a phenyl group, as in Scheme 6, facing page 15.


Ph3P+(CH2)3OH
EtO−
Ph
Ph
Ph
EtO−
Ph
Ph
OEt
-Ph
Ph
Ph
Ph
OEt
EtOH
Ph2(EtO)P+(CH2)3OH
EtO−
Ph2P(O)(CH2)3OH

SCHEME 6

N.B. In this thesis no attempt will be made to distinguish between the Berry or Ugi concepts in any particular case and the term pseudo-rotation will be applied to either.

Formation and Decomposition of Phosphoranes

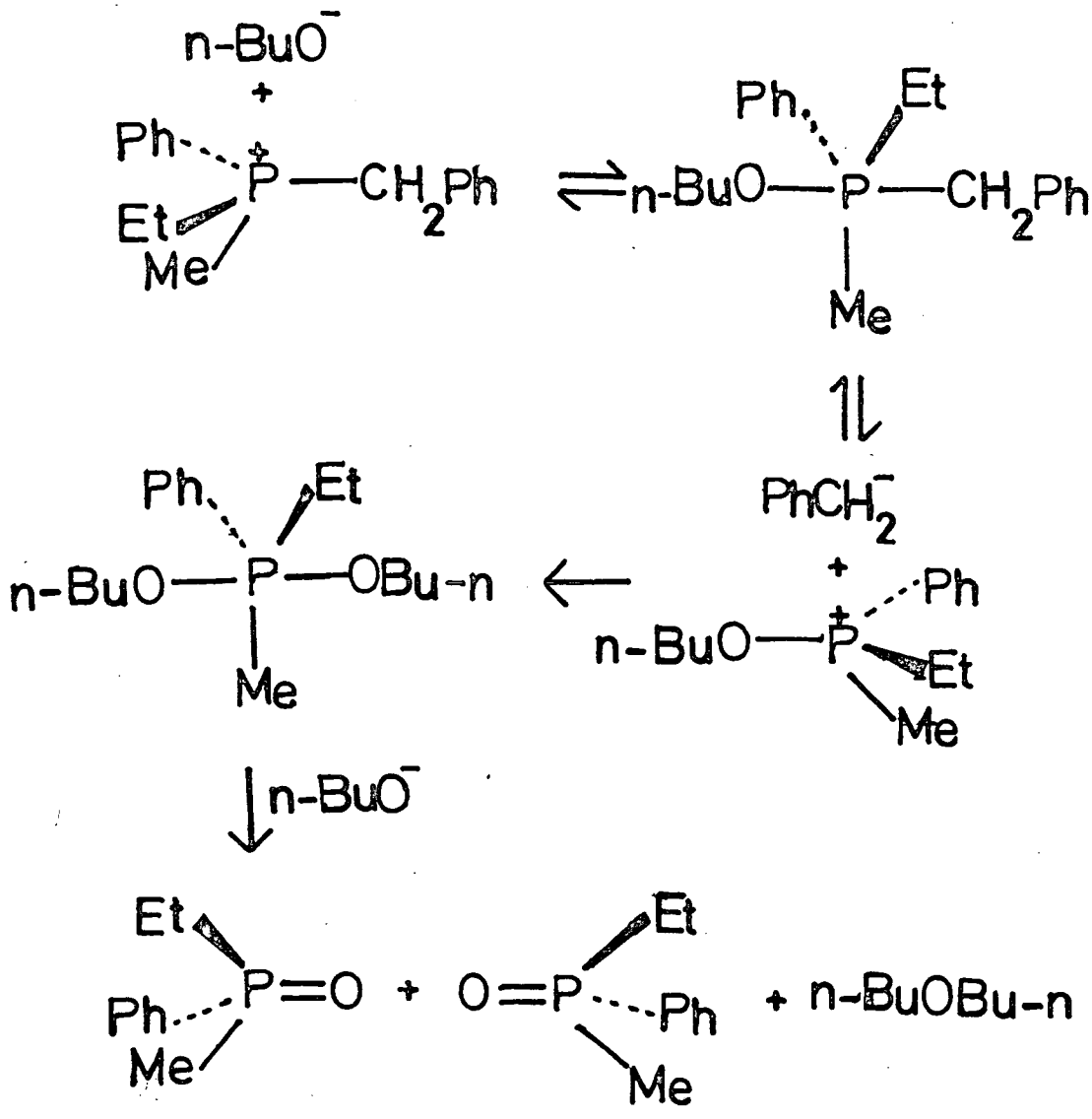
Ingold et al[34,35] developed a mechanism for SN2 displacements which involves apical attack of nucleophile and apical loss of departing anion in a trigonal bipyramid. This concept was taken further by McEwen et al[15,16,36] in a series of papers. A mechanism was proposed for the hydrolysis of phosphonium iodides, involving a pentacovalent intermediate, and ionisation of this intermediate was proposed to be rate determining, in contrast to Ingold[35] who suggested the rate determining step was the initial addition of hydroxide ion.

Methylethylphenylbenzylphosphonium iodide was found to undergo reaction with hydroxide ion with inversion of configuration. As the steric arrangement of the phosphonium iodide is a tetrahedron the hydroxide ion can attack either at a face or at an edge of this tetrahedron. Observation of complete inversion implies that attack occurs only via the face opposite the leaving benzyl group, i.e. apical attack and apical departure.

Further reactions of methylethylphenylbenzylphosphonium iodide have shown that the relative ease of elimination of various groups parallels their stability as anions, hence preference for loss of benzyl, and, again in contrast to Ingold, is influenced by the nature of the other groups.

Decomposition of methylethylphenylphosphonium n-butoxide gave racemised products with only a slight favour to inversion.

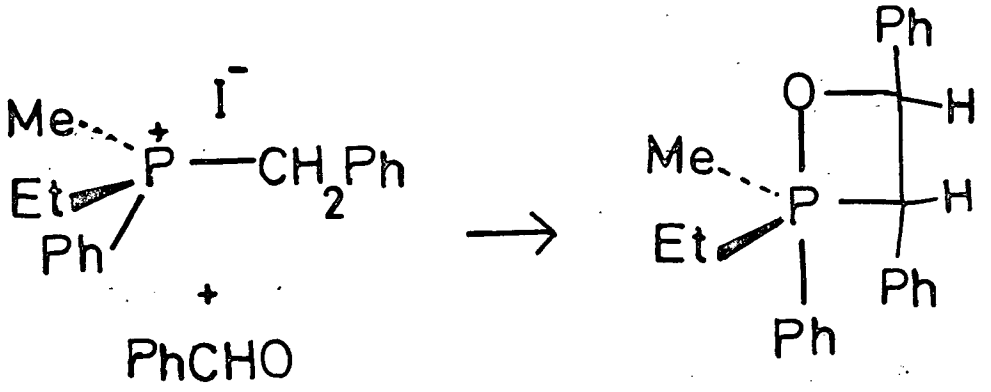
This was rationalised in terms of apical entry and departure as in Scheme 7.



SCHEME 7

Addition of styrene proceeded via a pentavalent oxaphospholan which was stable enough to allow ligand isomerisation and hence apical departure of a variety of ligands to give several oxides, some with retention and some with inversion. Wittig addition of benzaldehyde gave complete retention of configuration, the reaction proceeding as in Scheme 8 via a pentacovalent oxaphosphetan . Retention of

configuration occurs as the ring cannot take up high energy diequatorial arrangements which would be required to cause inversion by apical departure.



SCHEME 8

Ramirez[20] has noted that apical bonds are easier to form and break being longer and weaker (having smaller force constants) than equatorial bonds and further that equatorial entry would require the nucleophile to enter at the edge of the tetrahedron, as mentioned previously. This would result in severe steric crowding between the entering nucleophile and the other ligands so disfavouring such entry.

The concept of apical entry and departure has now been widely accepted and has been useful in rationalising many reaction schemes. However, Ramirez[20] has suggested that any set of conditions which allows departure of an apical ligand without charge separation should facilitate the decomposition of phosphoranes, while there is a fair amount of literature, which will be mentioned later, where, because of restrictions caused by ring effects, phosphoranes have decomposed via equatorial departure of a stable anion.

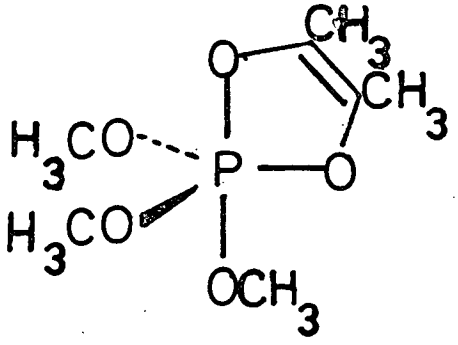
Apicophilicity and Apicophobia

Atoms, groups or molecules which have a tendency to take

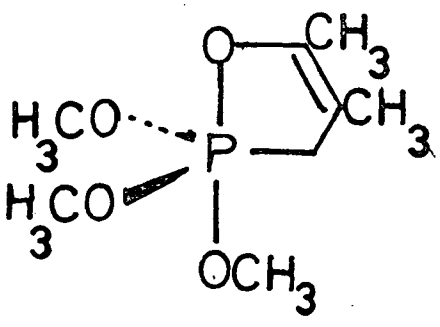
up apical positions on a trigonal bipyramidal skeleton are said to be apicophilic, while those preferring the equatorial placement are said to be apicophobic.

Muetterties[5] and Schmutzler[37] first recognised the concept when attempting to rationalise the ^{19}F spectral data for a series of mono-, di-, and tri-substituted phosphoranes. It was observed that the more electronegative fluorine atoms preferentially occupied the apical positions while the more electropositive alkyl or aryl groups entered the equatorial positions. In the mono-substituted cases, for example, rapid ligand isomerisation was observed, the alkyl or aryl group acting as the pivot group, while in the di- and tri-substituted cases, ligand exchange was inhibited, showing the preference of alkyl or aryl groups for the equatorial position, as any isomerisation must lead to placement of such a group in an apical situation.

Similar observations with pentacovalent dioxaphospholans and oxaphospholans (23 and 24), have been made by Westheimer.[6]



(23)



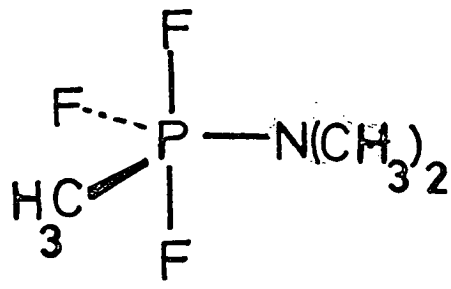
(24)

Compound (23) was found to give only a single methoxyl signal in the N.M.R. spectrum, even at -100°, implying rapid pseudo-rotation, whereas the spectrum of (24) is temperature dependent.[38] Westheimer proposed that this was due to restricted pseudo-rotation in (24) as,

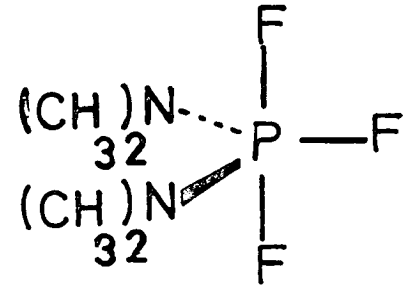
using the alkyl group as pivot would lead to a diequatorial ring with concomitant increase in strain[39] as mentioned earlier, while use of an equatorial methoxyl group as pivot would place the endocyclic alkyl group in the apical position.

The observations by Ramirez,[20] that oxaphosphetan pentacovalent species are locked such that the ring oxygen is apical, have already been mentioned, p.9 , as have the results of Denney[8], that the phospholenes (3) and (4) react via phosphoranes with apical oxygens in preference to an axial/equatorial ring placement.

Hudson[40] has observed apical placement of nitrogen although nitrogen containing groups have been shown to prefer the equatorial positions in trifluorophosphoranes. Muetterties[5] and Schmutzler[41] have observed no isomerisation, either by regular or irregular processes in (25) and (26) respectively.



(25)

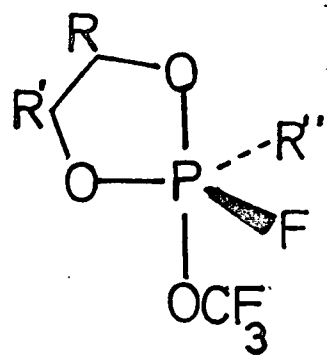


(26)

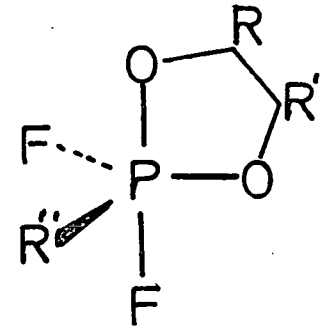
Ramirez[20] has stated that in most cases the apicophilic ligands are the most electronegative, in agreement with Muetterties polarity rule, but adds, however, that this is a rough guide if this is the only ligand property considered. Indeed, Muetterties[5] himself observed rapid exchange of the fluorine atoms in (1), showing that the preference of the fluorine atoms for apical positions could be overcome by relief of ring strain in moving from A to B as shown in Scheme 2, even though this places an

alkyl group in the unfavourable apical position.

Denney[42], in a neat demonstration of the competitive effect of the "element" effect against "strain" effects, reacted a series of 1,3,2-dioxaphospholans with trimethyl hypofluorite to give phosphoranes of type (27) which decomposed to (28).



(27)



(28)

When R=R'=H and R"=Ph or OMe, the fluorines were found to become equivalent and the oxygens interchanged, showing that the fluorines could be diapical, diequatorial or apical/equatorial, the "strain" effect competing with the "element" effect. However, when R=R'=Ph and R"=OMe or, when R=Me, R'=H and R"=OMe the pseudo-rotation was restricted to those isomers where the ring is apical/equatorial and the fluorines at best can be diequatorial or apical/equatorial. Here then, the "element" effect of the fluorines is not strong enough to overcome the combined "strain" effect of the ring and the "element" effect of the ring oxygens, although as has previously been mentioned, if the ring is carbocyclic, the "element" effect overcomes the "strain" effect of the ring and the ring can flip to the diequatorial placement, p.[8]. Where there is no "strain" effect as in the pentacovalent phosphorinan-

(17), the "element" effect is unopposed and no isomerization takes place, even up to 100°.

Debruin,[43] in the alkaline hydrolysis of a series of cis- and trans-1-X-1-alkoxy-2,2,3,4,4-pentamethylphosphetanium salts, observed an unusual order of apicophilicities, the ability of the ligands to switch from equatorial to apical positions being in the order Me_2N<OMe≃OEt≃O-i-Pr<SMe<Cl, not the order of electronegativity.

Oram and Trippett[19] in an attempt to quantify the preference of electronegative groups for apical positions found that apicophilicity is a balance between electronegativity, increase of which leads to apical tendencies, and ability to back bond to phosphorus d-orbitals, leading to equatorial tendencies, while remembering that both electronegativity and p_π-d_π bonding are dependent on other substituents and it is therefore unreasonable to expect one general scale of relative apicophilicities to apply in all cases. Steric effects, indeed, may also be involved.

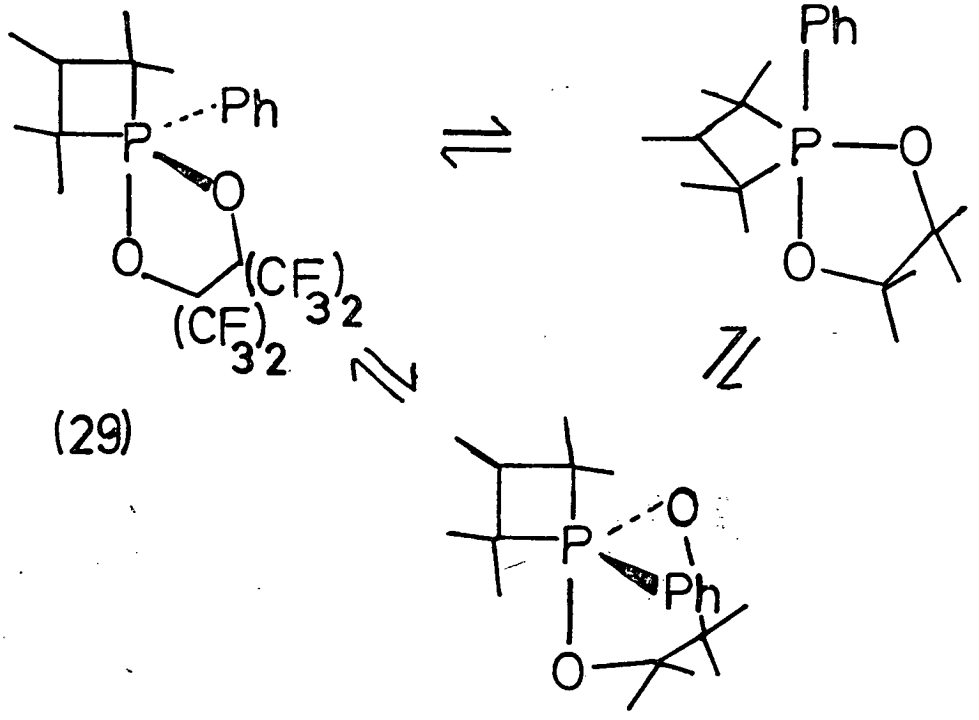
Emsley[44] has suggested, in fact, that the concept of a ligand being less apicophilic, the stronger the ability it has to act as a π-donor, is a more powerful one than electronegativity as Hinze and Jaffe[45] shown that electronegativity can vary widely with valence state, and in any case, atoms in a molecule tend to the same electronegativity. The ability to form p_π-d_π bonding should parallel the Lewis basicity,[44] to which the apicophilicity is then inversely proportional, which, adding the special case of the phosphonyl group (P=O) where p_π-d_π bonding is paramount, gives the apicophilicity scale P=O<<P-NMe_2<P-O<P-S<P-Cl as DeBruin observed.

Apical Alkyl Group vs. Diequatorial Ring?

While several examples of ring containing phosphoranes have already been mentioned where ring strain overcomes the tendency of alkyl groups to be placed equatorially, no mention has yet been made

of any relative energy barriers to placing an alkyl group apical against that of placing a ring diequatorially.

Oram and Trippett[19] have presented evidence for the intermediacy of a diequatorial phosphetan ring in the isomerisations of phosphoranes of type (29) as shown in Scheme 9.



SCHEME 9

The free energy of activation for this process was found to be 82 kj. mol^{-1}, which is the energy difference between the diequatorial and apical/equatorial ring placements, plus the difference in apicophilicity between phenyl and CMe_2, and possible steric effects.

Gorenstein[38,45] has observed restrictions to pseudo-rotation due to ring strain and the apicophobia of alkyl groups. He has noted, also, that the barrier to apical alkyl groups can be overcome, though this involves a barrier of 40-70 kj. mol^{-1}.,

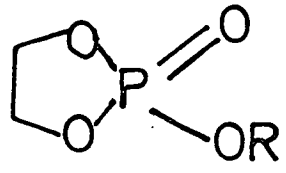
while placing the ring diequatorial requires about 84 kj. mol^{-1}. in agreement with Oram and Trippett. Ring opening and recombination reactions were noted at higher temperatures and these were found to require similar energy input to the diequatorial ring, although they occur only slowly.

From these values it would seem likely, that phosphoranes having apical alkyl groups would be easier to prepare than phosphoranes with diequatorial rings, and certainly, if conditions in a phosphorane are such that the ring can be placed diequatorially then, apart from steric considerations, there seems little against an apical alkyl group in the same phosphorane. The figures also confirm the observation[20] that oxaphospholane rings will place the endocyclic alkyl group apical rather than pseudo-rotate to a diequatorial position.

Ring Retention vs. Ring Opening

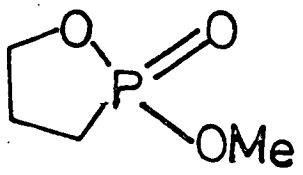
Ramirez[20] has observed that transformations of five-membered cyclic oxyphosphoranes into tetraco-ordinate phosphates generally proceed with ring retention during hydrolyses with limited amounts of water, and notes that the tendency for preservation of such rings may be obscured by rapid secondary reactions among the initial products, a cyclic phosphate ester, for example, having retained the ring during the original hydrolysis being subsequently transformed into an acyclic phosphate.

Westheimer,[6] in his earlier review of the hydrolysis of cyclic phosphate esters, has noted that while ring retention occurs in a series of esters such as (30), in the phosphonate (31) hydrolysis yields almost exclusive ring opening, which



R = H, Me, Ph.

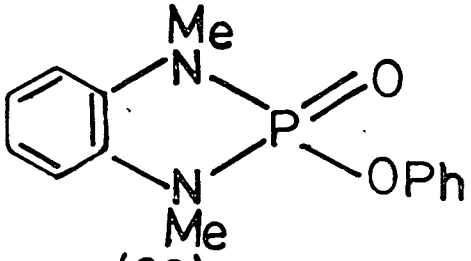
(30)



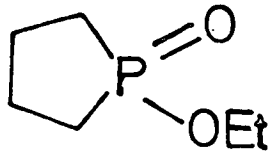
(31)

is explained in terms of restricted pseudo-rotation forcing the ring oxygen atom to be colinear with the phosphorus atom and the entering hydroxyl group, thus giving ring cleavage.

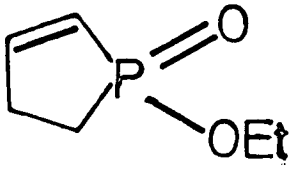
The diamidate (32) has been shown to retain the ring on hydrolysis,[47] as have the phosphinates (33-35), although, in contrast to all the examples cited previously, they show no acceleration compared to their acyclic analogues.



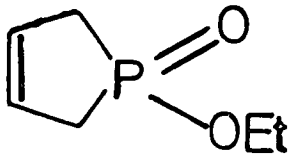
(32)



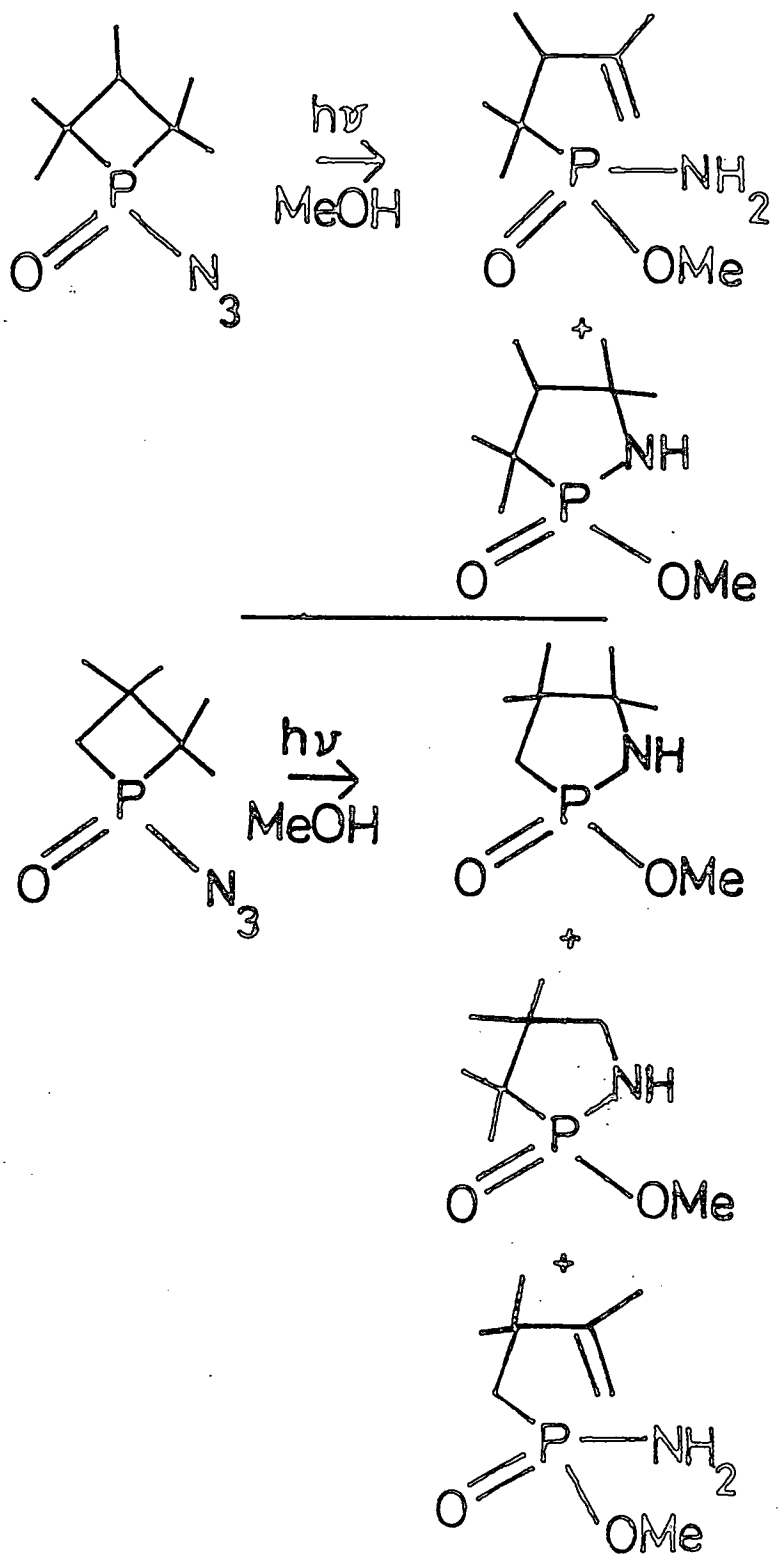
(33)



(34)



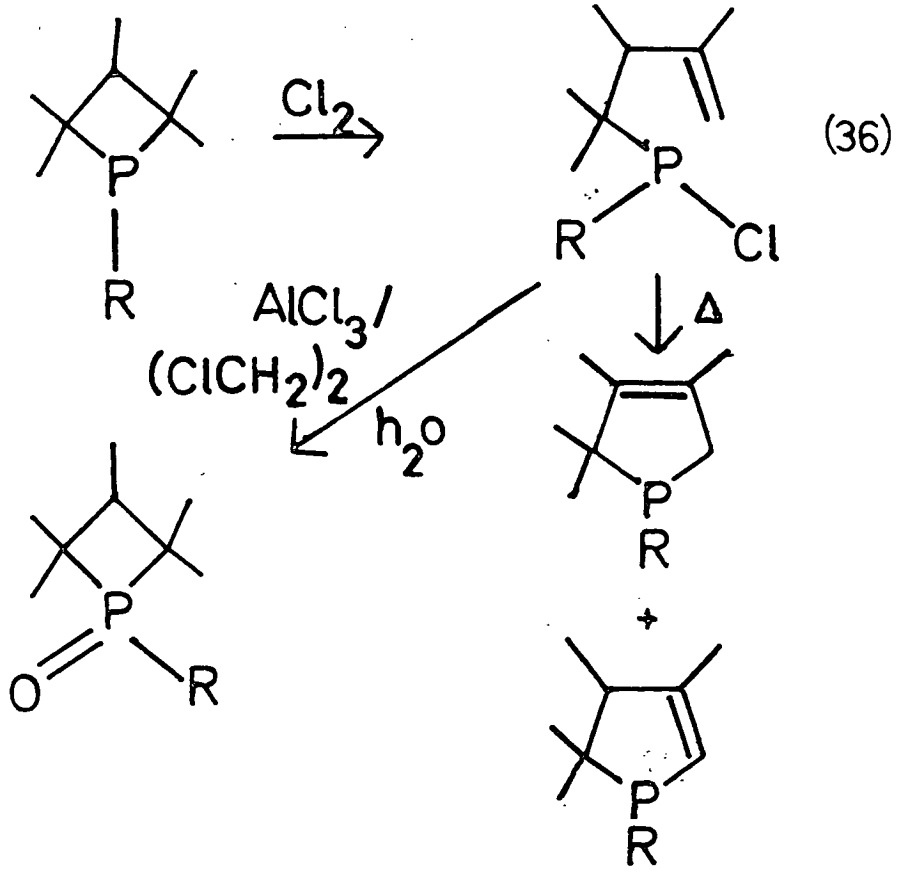
(35)



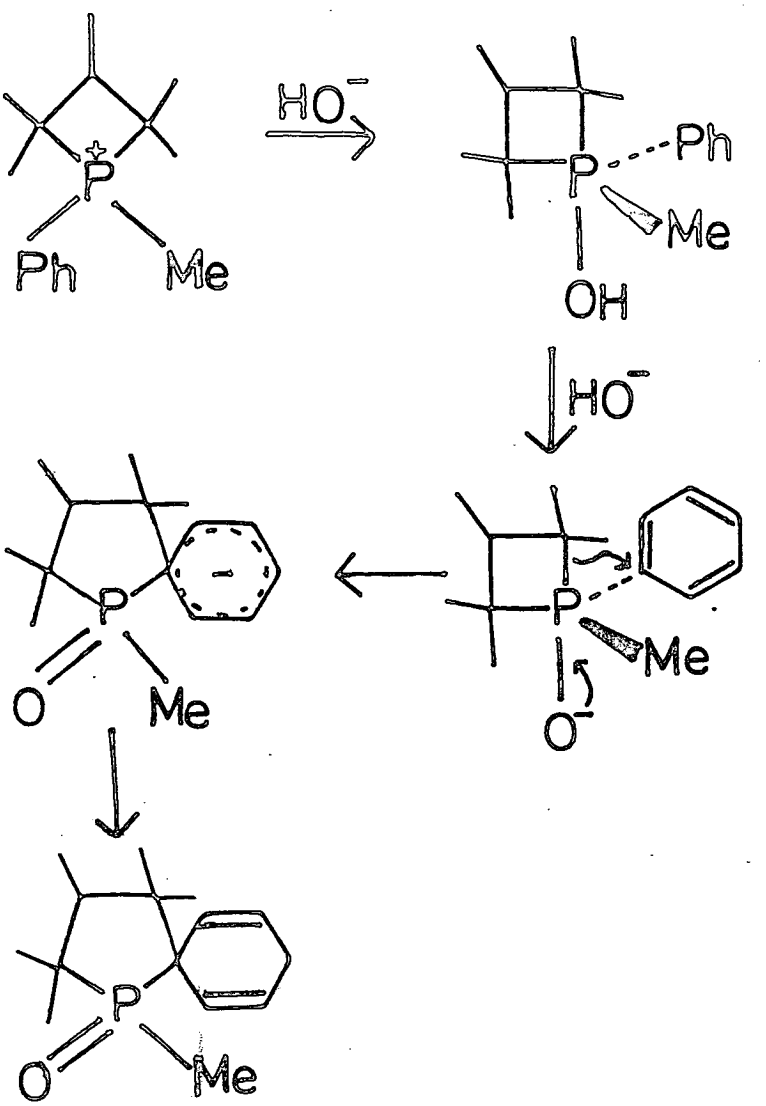
SCHEME 10

This latter result was explained[6] as being due to the inability of the phosphinates (33-35) to form a low energy phosphorane, as either the ring must be diequatorial or an alkyl group must be placed apically for the reaction to proceed, and in comparison to the oxy- and aza-phosphoranes, these will be of higher energy and hence the lack of acceleration in rate.

On the other hand, the observed ring cleavage in the phosphonate (31) due to the locked position of the ring suggests that phosphetans, in which the four-membered ring shows marked preference for the apical/equatorial position, as mentioned previously, will tend to ring open. In practice a mixture of ring retention reactions and ring opening reactions have been observed. Harger[48] has observed ring cleavage and ring expansion in the photolysis of 1-azidophosphetan-oxides in methanol, as shown in scheme 10 (facing page) while Trippett[49] has shown that reaction of phosphetans with chlorine or bromine yields the acyclic but-3-enylhalogenophosphines (36), as shown in Scheme 11,



SCHEME 11



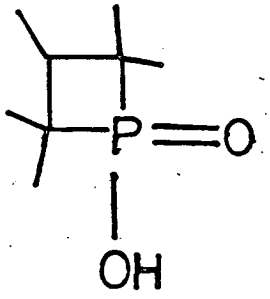
SCHEME 12

which then recyclise to phospholenes on heating or treatment with further halogen, and to phospholenes and/or phosphetan oxides with aluminium chloride.

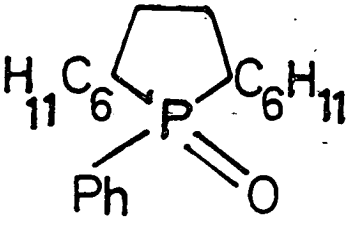
Trippett[50] has also observed ring expansion in the hydrolysis of 1-phenyl-1,2,2,3,4,4-hexamethylphosphetanium salts as in Scheme 12 (facing page) where the initially formed phosphorane undergoes a rearrangement.

The 1-phenyl-1-benzyl derivative, however, underwent hydrolysis and Wittig reactions with ring retention, to give the phosphetan oxide. This was explained as due to the greater stability of the departing benzyl anion in the latter case, compared to phenyl anion in the former, where rearrangement is then preferred.

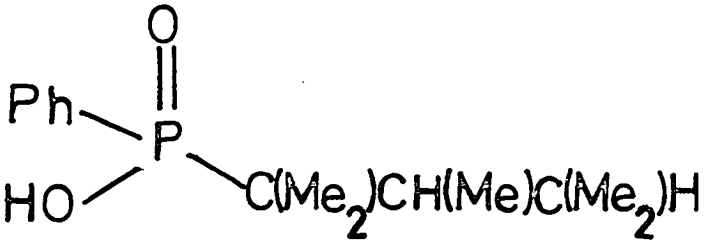
Ezzell[51] confirmed this suggestion when he observed that 1-benzyl-2,2,3,4,4-pentamethylphosphetan oxide, when fused with sodium hydroxide gave only the cyclic and acyclic acids (37 and 38) in the ratio of 1:4, showing preferential ring cleavage.



(37)

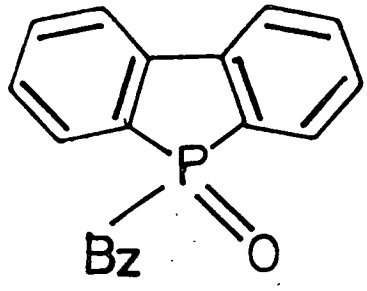


(39)

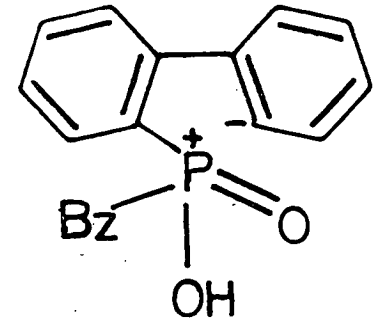


(38)

The influence exerted by the ring on the mode of cleavage in these reactions is in agreement with that observed for unsaturated five-membered rings[52] but in contrast to that of the saturated five-membered rings.[6,53] That the mode of cleavage is difficult to predict is suggested by comparison of the cleavage of 1-phenyl-2,5-dicyclohexylphospholan oxide (39, p.26) and the 1-phenyl-2,2,3,4,4-pentamethylphosphetan oxide mentioned earlier. Both these molecules have exocyclic phenyl groups and ring cleavage would give carbanions of similar stability. Ring cleavage, however, is only observed for the four-membered ring. On the other hand, the stability of the departing carbanion does have an effect when considering the cleavage of 5-benzyldibenzophosphole-5-oxide (40) and the 1-benzyl derivative of pentamethylphosphetan oxide. Here, both molecules have exocyclic benzyl groups, and though strain in the phosphetan is greater this reacts by exclusive exocyclic cleavage but the dibenzophosphole preferentially reacts by ring cleavage to give the resonance stabilised carbanion (41).



(40)

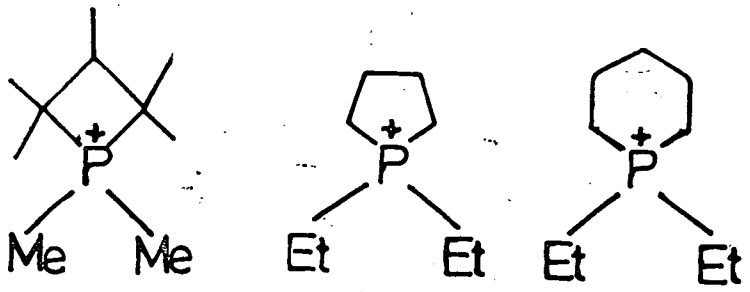


(41)

Marsi[54] considered that, in cyclic saturated systems containing phosphonium phosphorus as the sole hetero-atom, the reason that no ring cleavage had been observed, except in the highly strained phosphetan case, was due simply to the fact that in all cases the

leaving groups employed had been benzyl, phenyl, or alkoxyl which are all much more stable anions than would be formed from the aliphatic ring. He therefore studied a series of saturated cyclic phosphonium salts where the leaving groups were of comparable leaving ability to the ring carbons attached to phosphorus, e.g. Me or Et.

The 1,1,2,2,3,4,4-heptamethylphosphetanium salt (42) gave almost exclusive ring opening, while the 1,1-diethylphospholanium salt (43) gave 96% ring cleavage, and the 1,1-diethylphosphorinanium analogue (44) gave twice as much retention of the ring as ring cleavage.

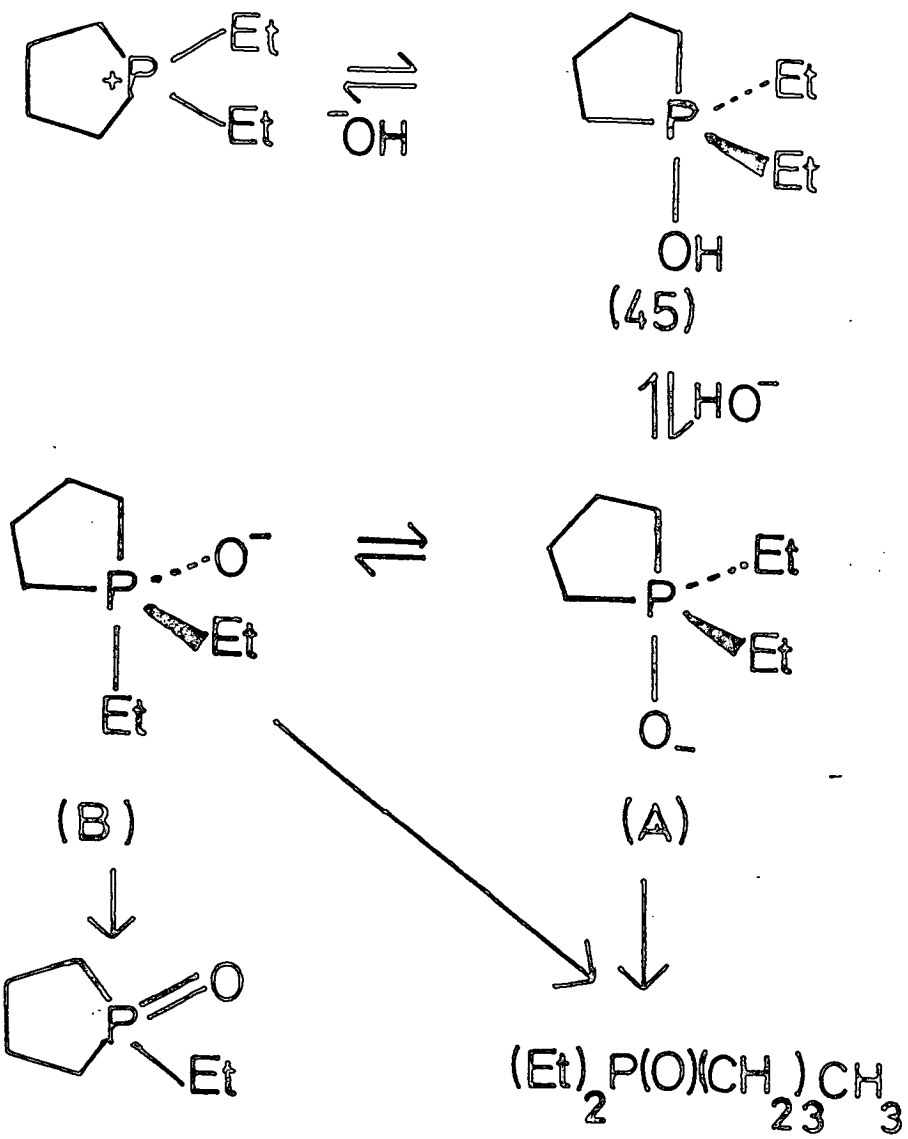


(42) (43) (44)

The dimethyl analogues of (43) and (44) however gave 3:1 ring retention for the phospholane ring and almost exclusive ring retention in the phosphiranan case.

It is interesting to note here that while the four-membered rings show ring opening and ring expansion capabilities, even in the presence of favourable leaving groups, here with $Me^{(-)}$ as leaving group a very little ring retention is still observed.

Ethyl was found to be cleaved in preference to methyl although for alkyl groups larger than methyl no preference is shown. This suggests, therefore, that in the case of molecules (43) and (44) equal amounts of ring opening and exocyclic cleavage should be observed. The six-membered ring, however, exhibits markedly less



SCHEME 13

ring opening while the five-membered ring cleaves almost exclusively. If formation of a phosphorane is postulated for the reaction, addition of hydroxyl to the phosphorus produces the phosphorane (45). Ring opening via the form A of this phosphorane, in scheme 13 (facing page) is then presumably favoured for the five-membered ring, rather than pseudo-rotation to B and loss of ethane with ring retention, although placement of the $O^{(-)}$ group equatorially does not contravene Muetterties' polarity rule, as $O^{(-)}$ is considered to be electropositive.

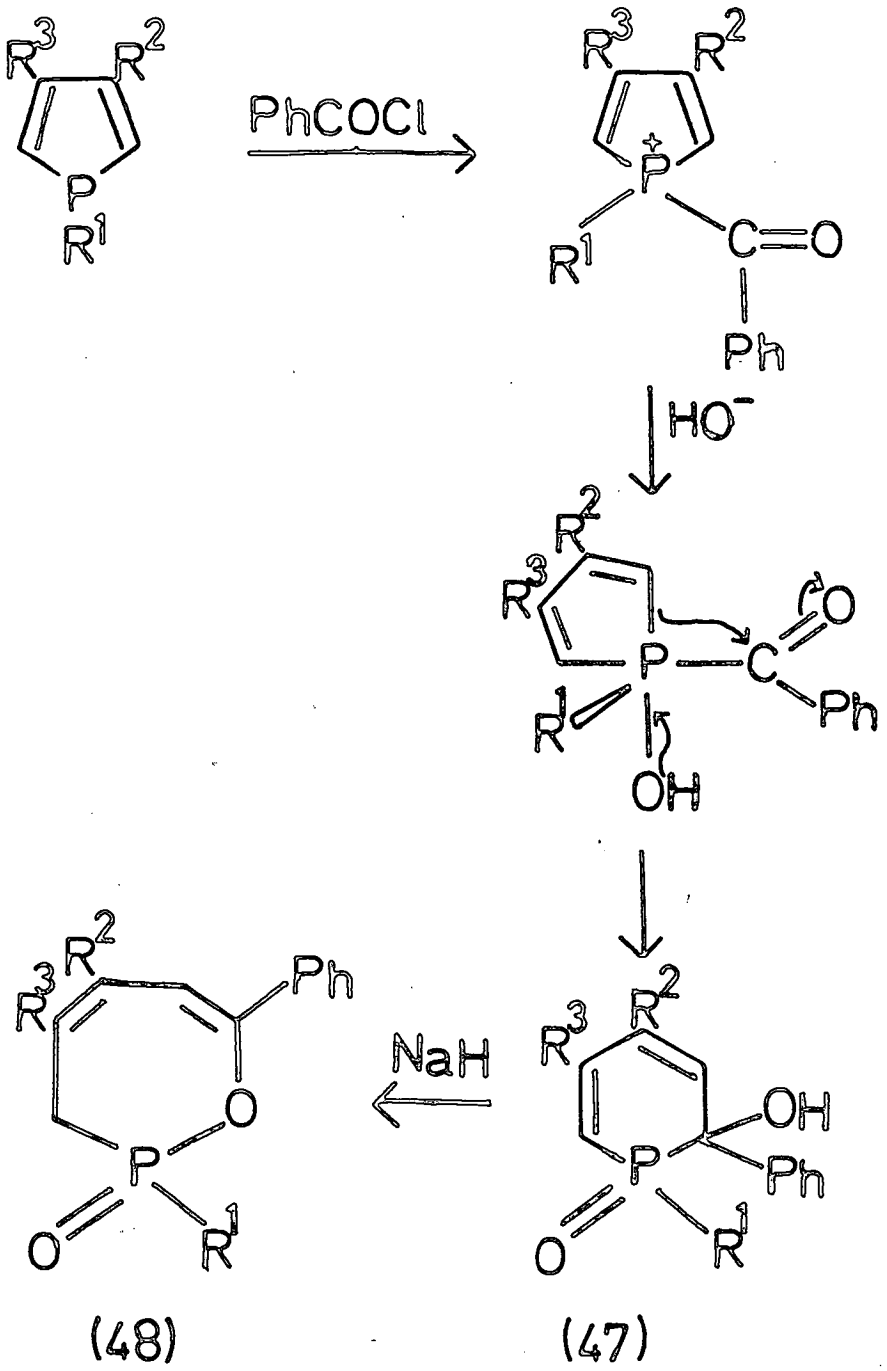
The predominance of ring retention is explained by the preference of the six-membered ring for diequatorial placement, as mentioned earlier, due to lack of strain effects, when loss of ethane from an apical position is much easier, and as apical placement of methyl rather than ethyl may be expected due to steric effects this can explain also the differences between the two derivatives.

The dimethylphospholanium salt analogue of (43) gave forty times more ring cleavage than was expected from comparison with data from its acyclic analogue, the dimethyl diethylphosphinium salt (46), while the dimethyl analogue of (44) resembled its acyclic analogue in 100% cleavage of the P-Me bond, evidence which would appear to back up the preceding suggestions.

$$(Et)_2\overset{+}{P}(Me)_2$$

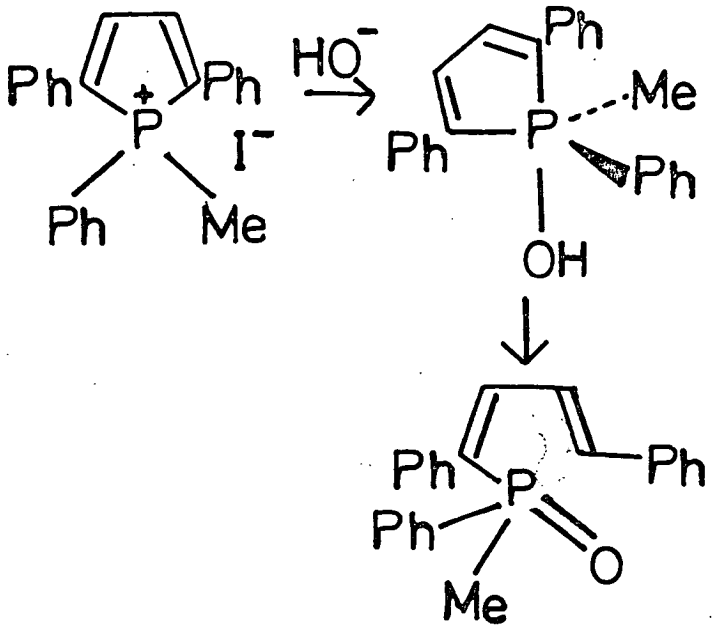
(46)

The influence of unsaturated five-membered rings on the mode of cleavage observed by Ezzell[52] has already been mentioned (p.27), due to the resonance stability of carbanions of form (41). The



SCHEME 15

alkaline decomposition of 1,2,5-triphenyl- and 1,2,3,4,5-pentaphenyl-phospholium iodides has been studied by Bergesen.[55] The reaction was found to proceed with ring cleavage, being first order kinetically in phospholium salt and first order in hydroxyl ion. The mechanism proposed involved formation of the unstable hydroxyphosphorane which ring opened with proton migration as shown in Scheme 14.

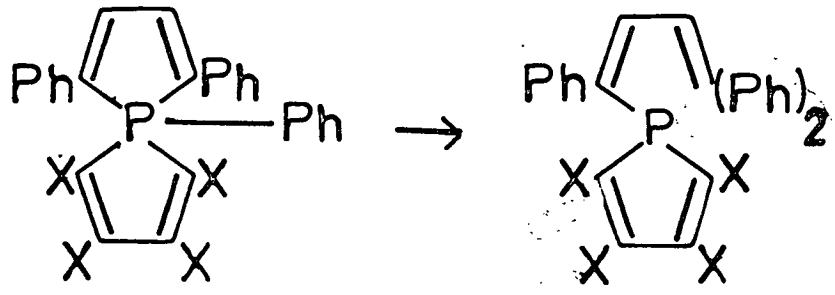


SCHEME 14

Mathey[56] has described a rearrangement, which also appears to involve a similar phosphorane, where treatment of certain phospholes with benzoyl chloride followed by an aqueous work-up gave 2-phenyl-2-hydroxyphosphorin oxides (47) as shown in Scheme 15 (facing page). The latter compound ring expands in the presence of catalytic quantities of sodium hydride to give a (7-phenyl)-1-oxa-2-phosphacyclo-hepta-4,6-diene (48).

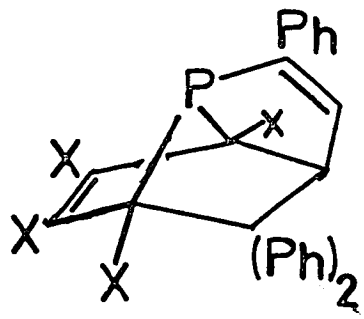
This reaction was not observed however for R^1 = tert-butyl, attack of hydroxyl in this case being followed by a 1,2 shift of the benzoyl group.

Hughes and Uaboonkul[57] proposed the spiran structure (49) for the 2:1 adduct of the reaction of 1,2,5-triphenylphosphole with dimethyl acetylenedicarboxylate. Warming the adduct was reported to give (51) via the ring opened intermediate (50) which then underwent an internal Diels-Alder reaction as shown.



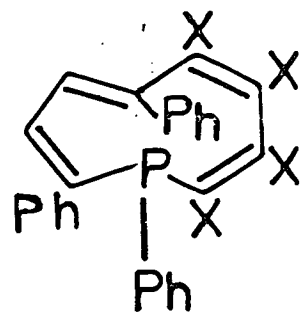
(49)
X=CO$_2$Me

(50)



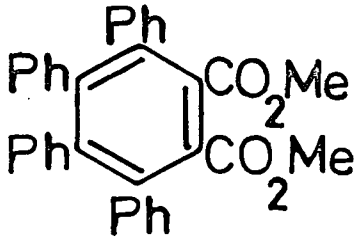
(51)

Tebby,[58] however, refuted this in a more detailed study, arguing that the intermediate is a zwitterionic species; the product found after the rearrangement being shown to be the nine-membered cyclic phosphine (52).

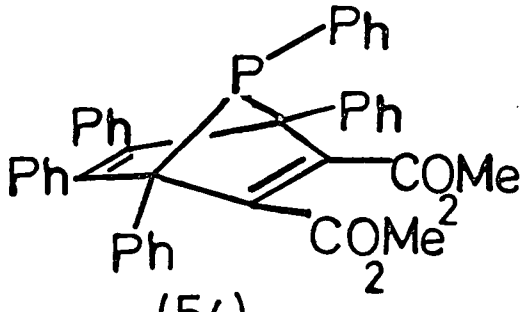


(52)

Phospholes have been shown to undergo other ring cleavage reactions, but most of these do not proceed *via* phosphorane intermediates. Braye, Hübel and Caplier,[59] for example, found that reaction of 1,2,3,4,5-pentaphenylphosphole with dimethyl acetylene-dicarboxylate in a sealed tube at 150° resulted in the formation of dimethyl 3,4,5,6-tetraphenylphthalate (53), presumably *via* the intermediacy of (54), with extrusion of the phosphorus moiety.



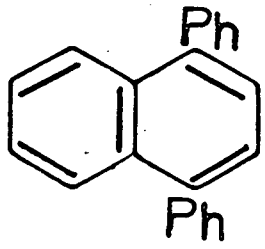
(53)



(54)

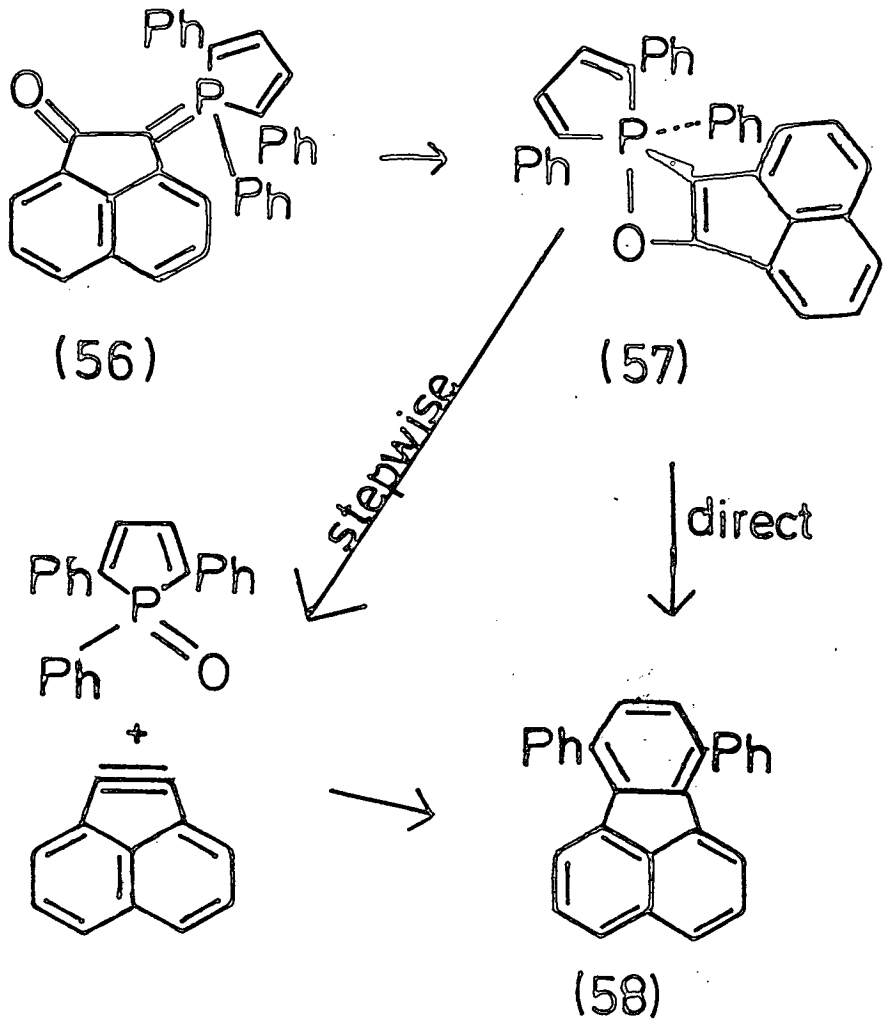
Campbell et al.[60] have reported similar reaction of 1,2,5-triphenyl-phosphole and its oxide.

Schmidt[61] observed extrusion in the reaction between 1,2,5-triphenylphospholes and benzyne, obtaining 1,4-diphenylnaphthalene (55) as product.



(55)

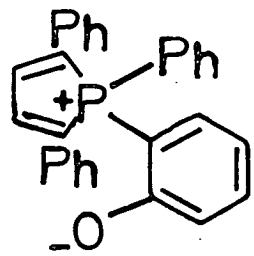
Cadogan et al.[62] reported similar reactions in the decomposition of the strained phosphole ylide (56) which suggests the phosphorane (57) as an intermediate transition species, where there would be relief of ring strain, which can then decompose directly or stepwise to



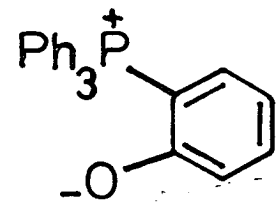
SCHEME 16

7,10-diphenylfluoranthrene (58) as shown in scheme 16 (facing page). Although the stepwise process is not supported by trapping of the aryne, alternative routes via intramolecular rearrangement or bimolecular reaction of (56) would require the ascent of severe steric barriers.

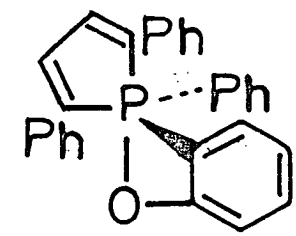
In a related system 1,4-diphenylnaphthalene (55) was obtained from the reaction of 1,2,5-triphenylphosphole with o-bromophenol, via the betaine (59), a result which was in contrast to the failure of the acyclic analogue (60) to give benzyne,[63] and which in comparison to Schmidt's work and the previous result suggests decomposition of the phosphorane (61) to the phosphole oxide and benzyne. On the other



(59)



(60)



(61)

hand, reaction of HBr with 1,2,5-triphenylphosphole oxide gave 1,4-diphenylnaphthalene while no reaction was observed in the absence of HBr or between the phosphole and HBr. As HBr is produced in the formation of the betaine (59) this is a further complication in the proposed scheme and no conclusions as to the actual mode of reaction have clearly been reached.

Conclusions

In this preliminary section it has been shown that pentavalent pentaco-ordinate phosphorus species are, however fleetingly or long-lived, intermediary in a wide variety of reactions involving nucleophilic attack at phosphorus. Further, it has been shown that

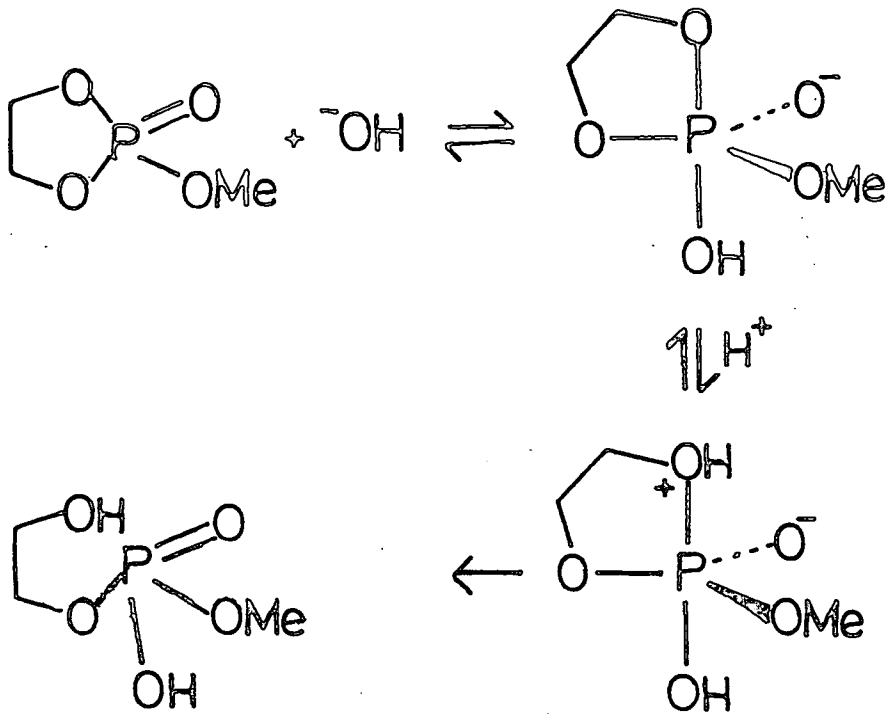
three-, four-, and five-membered rings can achieve relief of ring strain by apical/equatorial placement on the trigonal bipyramidal skeleton of such species, while six-membered rings, free of strain considerations are generally placed diequatorially.

On the other hand the preference of certain groups or atoms for the apical position has been shown and the competitive nature of the "element" against "strain" effects demonstrated, with the observation that ligand isomerisation on the trigonal bipyramidal skeleton can occur and by several types of process.

It has also been demonstrated that phosphoranes are formed and decomposed by apical attack and departure, and that this can in some instances lead to ring cleavage.

Finally, it has been shown that while ring retention is preferred in most cases, ring cleavage has been observed in a fair number of reactions. While ring cleavage is difficult to predict it has been observed that the ring size can influence the mode of cleavage in some cases, but that in others the major influence is the stability of the departing anion.

In the following section, further reactions of nucleophiles at phosphorus will be discussed in the light of these observations, and reasons for apparent anomalies will be discussed.

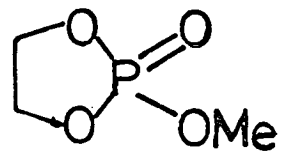


SCHEME 17

Nucleophilic Reactions at Phosphorus Involving Phosphoranes: The Effect of Such Species on the Kinetics, the Mechanism, and the Stereochemistry of the Reactions.

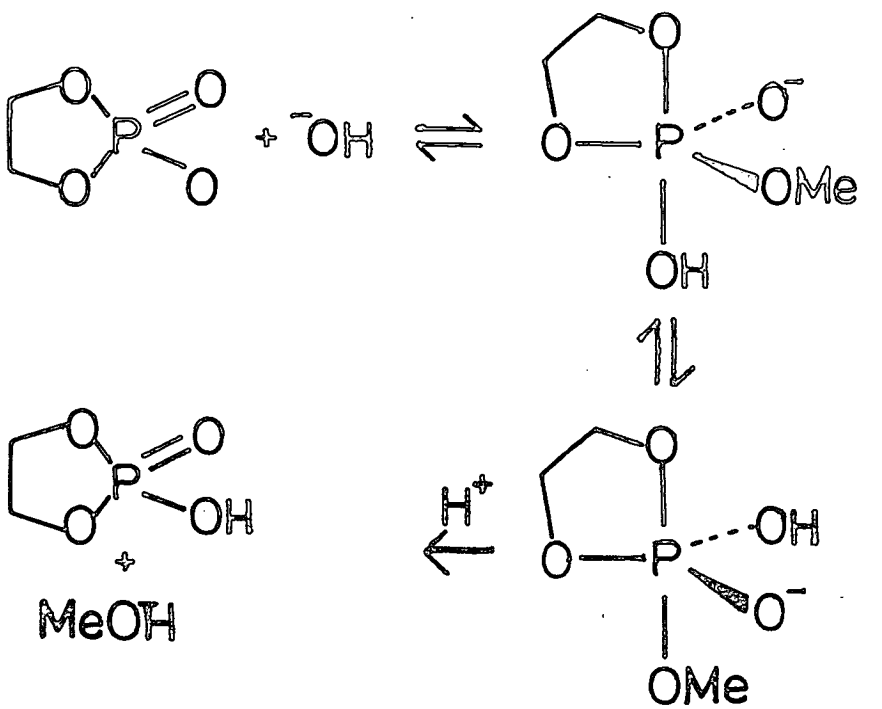
(a) Hydrolysis

Phosphate esters have been shown to behave differently in acid and alkaline solution. Haake and Westheimer[39] have shown that both phosphoryl oxygen exchange and ring cleavage occur in acid solution while only ring cleavage is observed in alkaline solution. Cadogan[64] has observed similar behaviour for O-methyl ethylene phosphate (62), acid hydrolysis giving a mixture of cyclic and open-chain species, while alkaline hydrolysis gave exclusive ring opening.



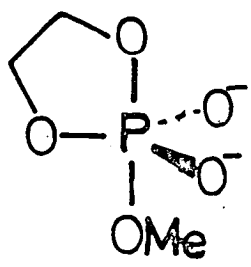
(62)

The behaviour can be explained[20] in terms of trigonal bipyramidal intermediates where, in acidic solution, the rate of hydrolysis with ring opening is proportional to the proton concentration, the reaction proceeding *via* the mechanism shown in scheme 17 (facing page) while the rate of permutational isomerism required for exocyclic hydrolysis *via* the mechanism in scheme 18 (facing page 36) is independent of the acid concentration. At high acidity therefore, the mechanism in scheme 17 is promoted and that in scheme 18, being dependent on the rate of permutational isomerism fails to keep pace with ring cleavage. In alkaline solution, not only is the mechanism in Scheme 17 disfavoured, a further reaction dependent on the square of the hydroxide ion concentration takes place, possibly *via* a hexaco-ordinate

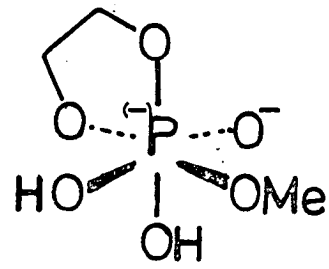


SCHEME 18

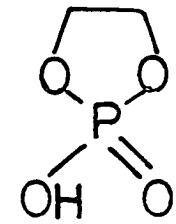
species (64).[20]



(63)

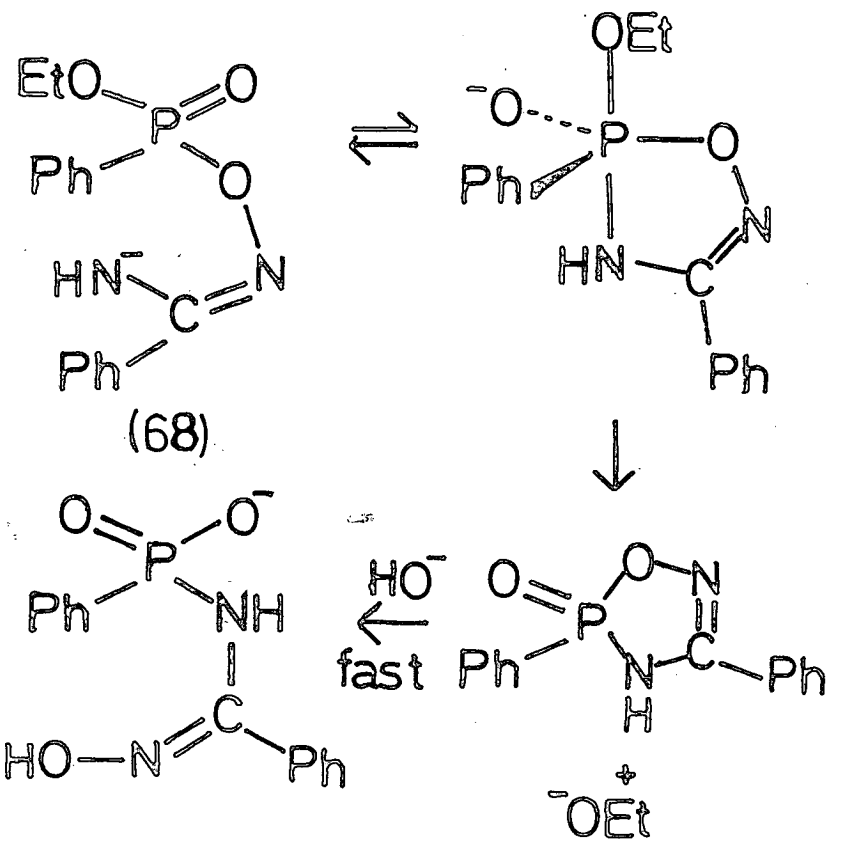


(64)



(65)

The hydrolysis of ethylene phosphate (65) in acidic medium is worth mentioning at this juncture. Here a slight tendency is observed towards collapse, of the intermediate oxyphosphorane, with ring opening, in apparent contradiction to previous comment. Following the same mechanism as given for the O-methyl analogue in schemes 17 and 18, the leaving group for ring retention here is seen to be H_2O while that for ring opening is methoxyl. In the O-methyl case the reverse is true and even at high acid concentrations a slight preference for ring retention is still observed. This suggests[20] therefore that methoxyl, being a better leaving group than water, controls the product ratio observed. Similar effects of leaving groups have been observed by Greenhalgh and Hudson[65] and Hudson and Woodcock[66], in the neutral and alkaline hydrolysis with n-butylamine of several phosphorylating agents and in the behaviour of phosphorylated, phosphinylated and phosphonylated benzamidoximes in alkaline solution respectively. Hence in the latter case three different mechanisms are observed. In the phosphonylated case (66) a Tiemann Rearrangement occurs, which is promoted as $(RO)_2PO_2^{(-)}$ is a good leaving group, as shown in scheme 19, (p.37).


EtO
O
P
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HN
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(68)
OEt
O
P
Ph
O
N
HN
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HO⁻
fast
O
O⁻
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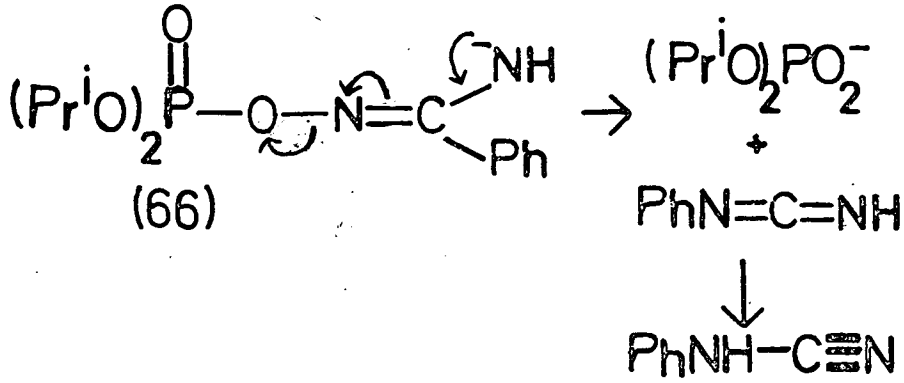
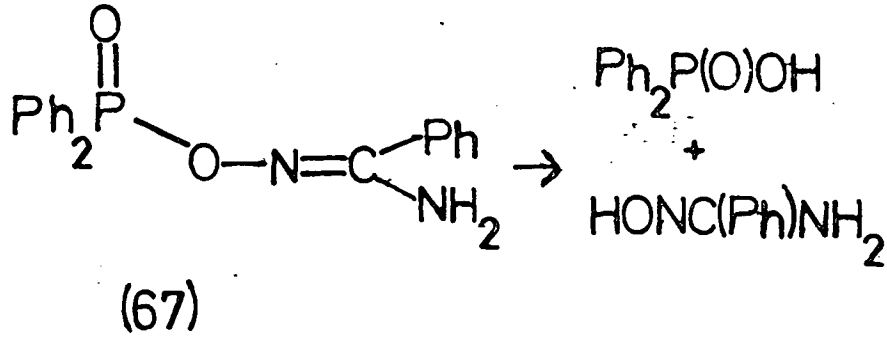
SCHEME 20



SCHEME 19

The phosphinylated benzamidoxime (67) undergoes a standard displacement, while the phosphonylated analogue (68) is a stronger



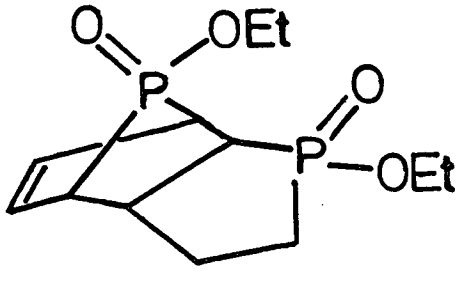
electrophile than the phosphinylated case and $RO(Ph)PO_2^{(-)}$ is a poor leaving group and so intramolecular nucleophilic attack on phosphorus is promoted to give a phosphorane intermediate as shown in scheme 20 (facing page).

The classic review of the hydrolysis of phosphate esters by Westheimer[6] has been referred to on several occasions previously, as has the more recent survey by Ramirez.[20] Kinetic results referred to in these papers have indicated that five-membered cyclic phosphate esters hydrolyse millions of times faster than their acyclic analogues. These results are neatly explained in terms of pentaoxyphosphorane trigonal bipyramidal intermediates with apical/equatorial rings, relief of ring strain causing the acceleration in rate and cleavage

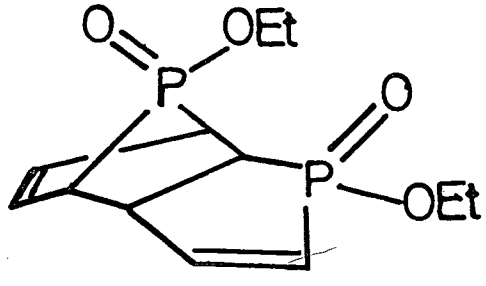
of the apical P-O bond giving ring cleavage.

The phosphonate (31) hydrolyses rapidly, as would be expected while the exclusive ring opening observed has been explained in the previous section.

A surprising result was noted, however, by Dennis and Westheimer,[47] who have shown that five-membered cyclic phosphinates hydrolyse slowly, showing little or no acceleration over their acyclic analogues. This they explained in terms of the formation of a trigonal bipyramidal intermediate where the placement of an alkyl group in the apical position, as would follow from the results above, is energetically unfavourable. On the other hand, they observed that 1-ethoxyphosphole-1-oxide was very reactive and this led them to believe that rate acceleration could be observed in such cases as the ring strain was sufficient to overcome the barrier to apical alkyl groups. Indeed they have since neatly demonstrated that this is the case[67] by showing that the highly strained phosphinic ester at the bridgehead, in compounds of type (69) and (70), hydrolyses some 10^5 times faster than the phosphinic ester in a phospholan or phospholene ring in the same molecule.



(69)

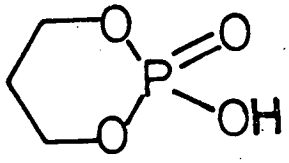


(70)

Oxaphosphetans have been observed[20] to hydrolyse rapidly with ring opening as would be predicted from the known "locked" apical/equatorial position of the ring and relief of ring strain. These same considerations, on the other hand, would suggest that

six-membered phosphate esters, free of strain, should not hydrolyse appreciably faster than their acyclic analogues, and Khorana et al.[68] have, indeed, shown this to be the case, while Asknes and Bergesen[69] have observed that the alkaline decomposition of five-membered ring phosphonium iodides occurs some 1300 times as fast as that of the corresponding six-membered ring analogue although they found this to be due as much to a greater "frequency factor" as ring strain, possibly due to the greater planarity of the smaller ring. The six-membered ring reacts at the same rate as the acyclic analogue.

Cox and Ramsay have found a 10^7 difference between the five- and six-membered rings in the hydrolyses of 2-hydroxy-2-oxo-1,3,2-dioxaphospholan (65) and the corresponding dioxaphosphorinan (71).

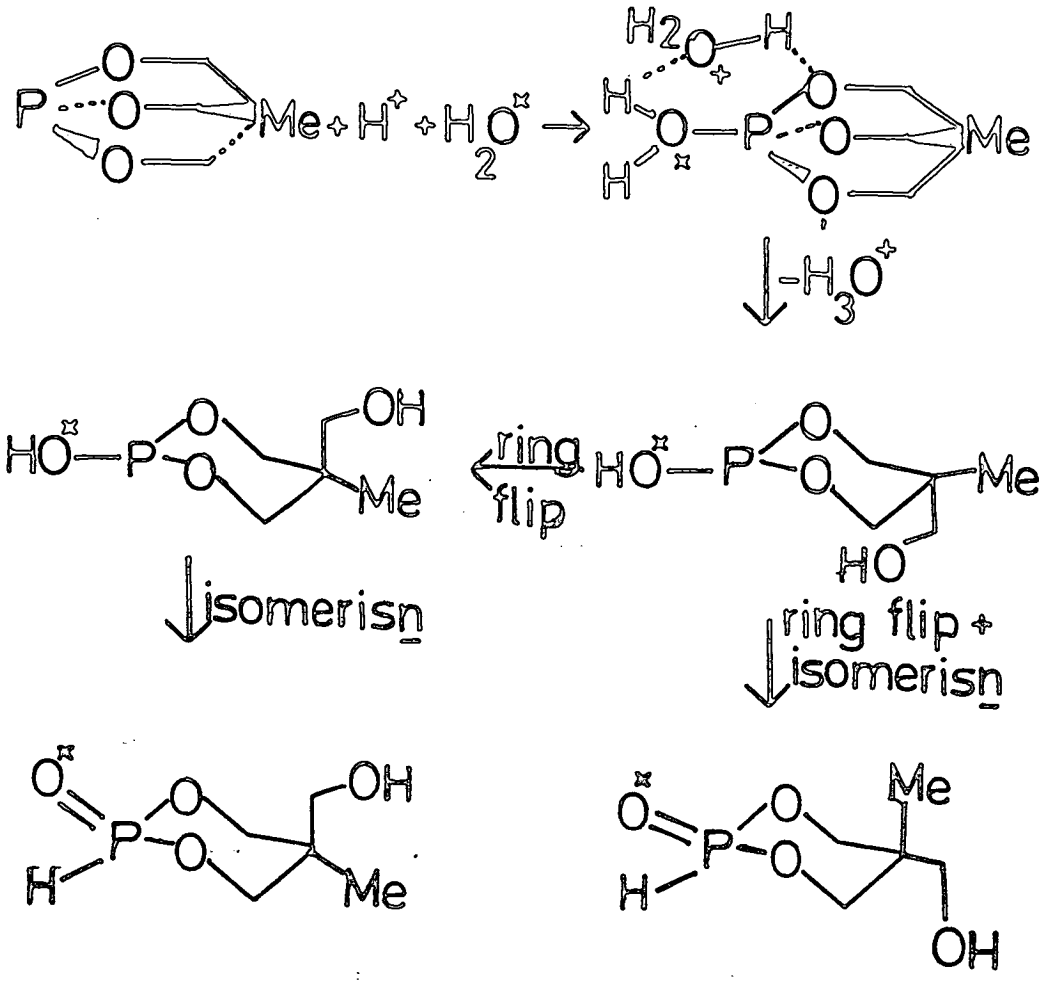


(71)

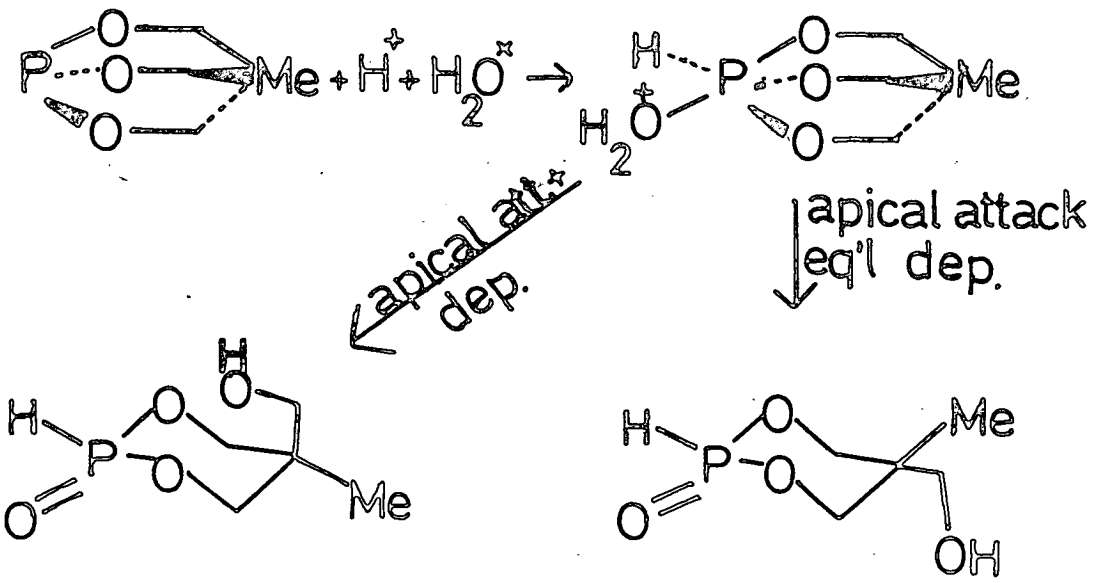
More recently, Cremer et al.[71] have found that the hydroxide decomposition of a series of six-, five-, and four-membered ring phosphonium salts shows a marked increase in rate in going to the smaller ring size, while six-membered ring compounds gave similar rates to acyclic analogues. They found, moreover, that the increase in rate was due to changes in the activation energy (since the more strained four-membered ring will be the least stable reactant; on formation of a transition state or intermediate phosphorane it will give as stable, if not more stable, such species, and will have the lowest activation energy) and changes in entropies. The change in entropy may explain the "frequency factor" effect found by Aksnes.[69]

Some discussion has, indeed, occurred as to the nature of the "strain" in question. Comparisons of the heats of hydrolysis of the various species involved suggest that ring strain of some sort is a major influence[6,20,72] but there are anomalies. Cremer's results[71] suggest that the change in activation energy is due to the ring strain. Gorenstein et al.[73] have calculated the angle and torsional strains in acyclic and cyclic phosphates and concluded that the high heat of hydrolysis of five-membered rings is associated to a significant extent with the relief of torsional strain and, whatsmore, that the preferred torsional conformations of acyclic esters are strongly coupled to the RO-P-OR bond angles. Any attempt then to separate the ring strain energy in cyclic systems into bond strain and torsional strain would be meaningless. Hudson,[72] on the other hand has suggested that the entropy factor noted by Cremer[71] causes part of the acceleration, direct evidence for ring strain being limited. He proposed that there is an increase in entropy in pentacovalent phosphorus transition species or intermediates associated with a "loosening" of the pseudo-rotational motion of the ring in such species, observing that the low nucleophilicity of trivalent phosphorus compounds may well be due to a decrease in entropy due to restrictions on such motion in the tetravalent species. Some support for this may come from Holmes[74] who suggests that a "loosening" of the ring occurs when in the apical/equatorial position due to the lengthening of one of the ring bonds along the apical axis.

Conclusions based on these premises however, are difficult to make as the rate of a reaction which is actually observed can be subject to a wide variety of constraints, and the premises above can only hold in any case if the rate determining step in the



SCHEME 21

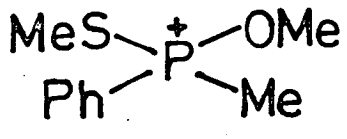


SCHEME 22

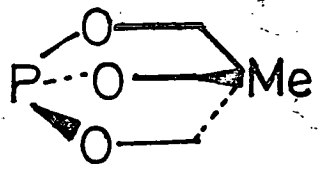
reaction in question is the formation of an intermediate phosphorane species.

Tebby,[75] for example, has noted that the alkaline hydrolysis of triphenylbenzylphosphonium hydroxide may be increased by a factor of more than 10^5 by reducing the water content of the medium, an acceleration remarkably similar to that observed by Westheimer.[67]

Furthermore, while Debruin[76] has explained his results from the hydrolysis of methylthiomethoxyphenylmethyl phosphonium salts (72) in terms of apical entry and departure of anions from a trigonal bipyramid, either before or after pseudo-rotation, McEwen et al have shown that the acid catalysed hydrolysis of (73) can be explained both in terms of the mechanism proposed by Aksnes[78] for



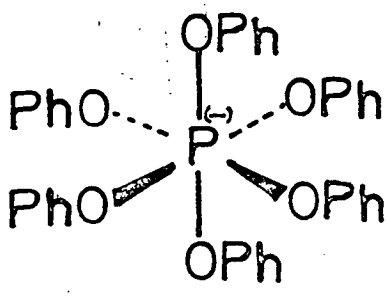
(72)



(73)

the hydrolysis of tripropyl phosphite as shown in scheme 21 (facing page) or <u>via</u> a pentaco-ordinate species as shown in scheme 22 (facing page), as the phosphoryl oxygen was shown by labelling to come from the water.

Westheimer[79] has shown whatsmore, that pentaco-ordinate species can themselves undergo further hydrolysis, the evidence favouring six co-ordinate species as intermediates, thereby complicating further the reaction mechanism, such six co-ordinate species being supported by the work of Ramirez[20] and Aksnes[33], while six co-ordinate species have recently been isolated by Ramirez[80] and by Munoz et al.[81], and Westheimer himself[82] has established the formation of the anion (74)

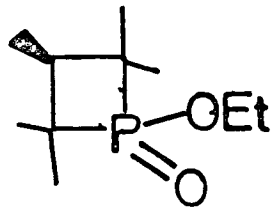


(74)

by ^{31}P n.m.r.

Steric Hindrance as a Constraint to Hydrolysis

Bergesen[83] has shown that the cis-isomer of 1-oxo-1-ethoxy-2,2,3,4,4-pentamethylphosphetan (75) hydrolyses in alkaline solution seven times faster than the trans-isomer, and suggested that this was due to the more favourable entropy of activation of the cis-isomer, which allowed reaction via the less sterically hindered pathway.



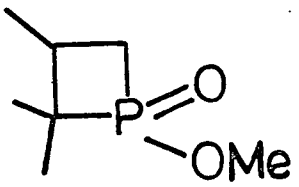
(75)

(76)

(77)

Hawes and Tripett[84] have confirmed this result and find that the four-membered ring has a similar rate of hydrolysis to acyclic analogues, which again, they suggested, was a result of competition between acceleration due to ring strain and retardation due to steric hindrance of attack at phosphorus by the α-methyl groups. This suggestion being supported by their observations that in the hydrolysis of molecules such as (76) and (77), where

where R=tert-Bu or iso-Pr, one alkyl group attached to phosphorus produces little hindrance to attack on phosphorus by hydroxide ion, while a second alkyl group produces a substantial decrease in reaction rate. Further evidence for such hindrance was the rapid rate of hydrolysis of 1-oxo-1-methoxy-2,2,3-trimethylphosphetan (78) where attack of the hydroxyl anion from the side next to the ring $-CH_2$ group is possible and no steric retardation is then seen, the difference in rate being some 4×10^3 in favour of the latter compound.



(78)

$(t\text{-Bu})_2P(O)Cl$

(79)

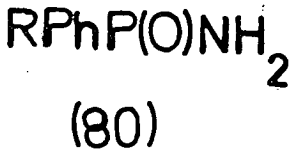
Trippett[85] has further shown that the pentamethylphosphetan oxides are stable to alkaline hydrolysis in 10 N sodium hydroxide at 100° while the 2,2,3-trimethyl- and 2,2,3,3-tetramethyl analogues are readily hydrolysed in refluxing 2 N sodium hydroxide to give ring opened acids. Again in contrast to the oxide, Cremer and Chorvat[86] have observed that the phosphetanium salt rearrangement shown in scheme 12 occurs rapidly in 1 N sodium hydroxide at 10°. (p.12)

Haake and Ossip[87] have shown that while displacement reactions can occur at phosphorus either by a dissociative or an associative mechanism, phosphorus exhibits a great preference for the associative mechanism, dissociation occurring in reactions of the sterically hindered di-tert-butylphosphinyl chloride (79) but not in the di-iso-propyl analogue. Haake et al[88,89] have shown, however, that steric inhibition of the associative mechanism occurs in pentamethyl-phosphetan oxides and have suggested indeed[90,91] that the observed

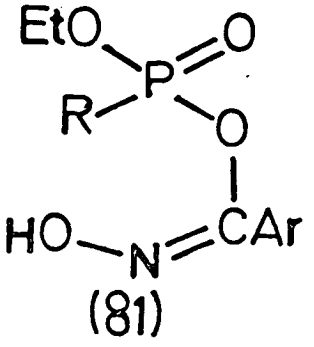
inhibition in rate of the amide and acid chloride of pentamethyl phosphetan in acid hydrolyses is due to a complete change in mechanism, displacement occurring *via* a direct SN2 process rather than an associative/dissociative pathway.

Hudson and Keay[92] have also observed steric retardation by bulky substituents at phosphorus, and Harger[93] has noted that the reaction of a series of alkylphenylphosphinic amides (80) gave liberation of ammonia, as expected, when R = cyclopropyl or ethyl but that stable, crystalline hydrochlorides were isolable when R = 1-methylcyclopropyl, isopropyl or *tert*-butyl, the stability of the latter materials being attributed to steric inhibition of attack at phosphorus by the relatively bulky alkyl groups, the rates found for hydrolysis being in accord with this explanation.

On the other hand, Cadogan and Eastlick[94] have shown from the alkaline hydrolysis of ethyl α-hydroxyimino-p-nitro-benzyl alkyl-phosphonates (81) that attack on phosphorus from an internal nucleophile is not subject to such steric constraints. Furthermore, models have suggested that the nucleophile may not only attack phosphorus from an apical position.



(80)



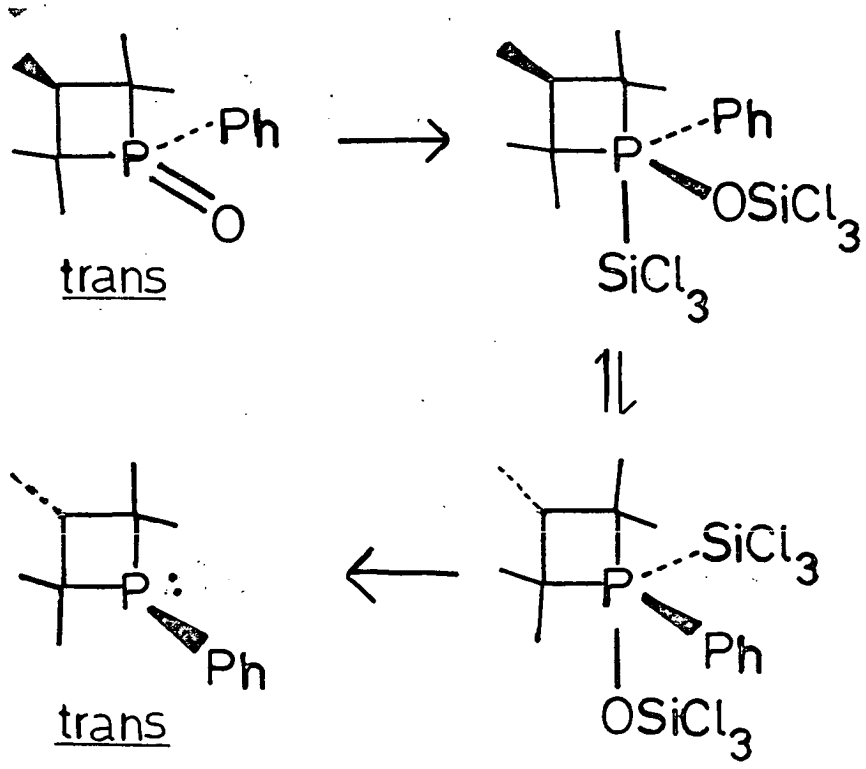
(81)

Ar=p-NO_2-C_6H_4-

Effects of Rings in Phosphoranes on the Stereochemistry of Reaction

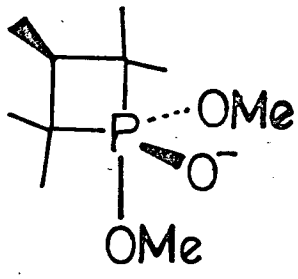
That acyclic phosphorus compounds undergo nucleophilic displacement reactions with inversion of configuration[36] has already been discussed, while the results obtained when pentacovalent phosphorus cyclic species are intermediate in the reaction between phosphonium salts and styrene and benzaldehyde have also been mentioned earlier.

Hexachlorodisilane is known[95] to deoxygenate acyclic phosphine oxides stereospecifically with inversion of configuration. Cremer[96] has shown that pentamethylphosphetan oxides (75) are deoxygenated, however, with complete retention of configuration, the likely pathway being that shown in Scheme 23.

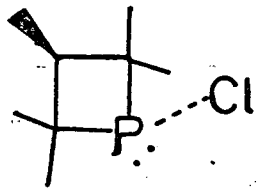


SCHEME 23

Hawes and Tripett[50] have shown that hydrolysis and Wittig reactions as well as a variety of other substitutions all proceed with retention of configuration in the phosphetan oxide system, an observation supported by further work of Tripett himself[97] and by Cremer[98], who observed retention of configuration in the attack of methoxide ion on either cis- or trans-1-methoxy-2,2,3,4,4-pentamethyl-phosphetan-1-oxide, presumably via a scheme similar to scheme 23 where the electropositive phosphonyl oxygen anion produced in the intermediate (82) must remain preferentially in the equatorial position and with the ring then limiting ligand isomerisation



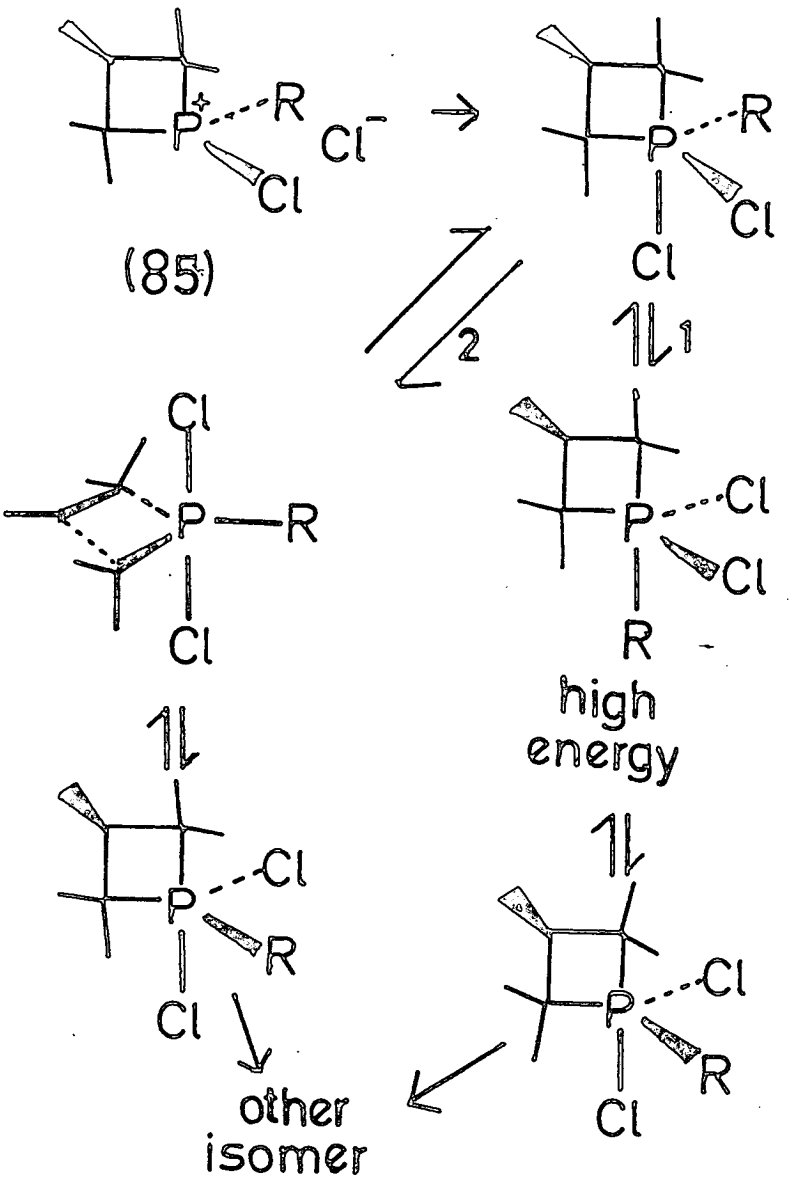
(82)



(83)

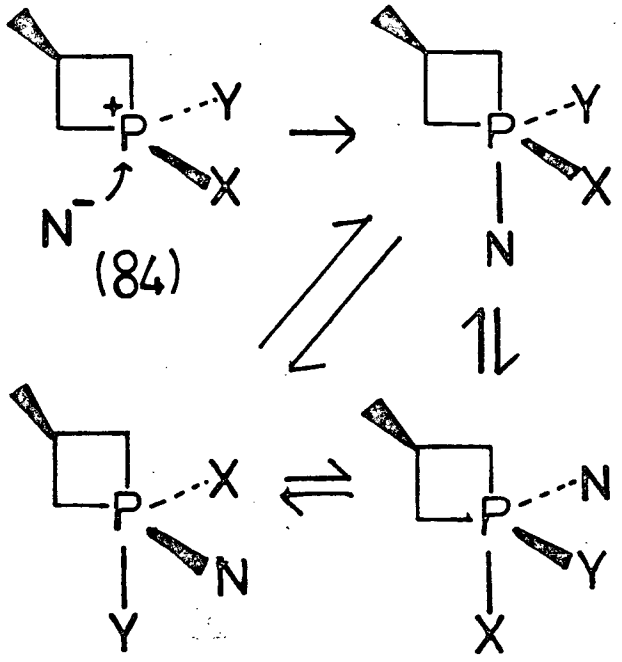
to switching of the methoxyl groups, retention of configuration is assured.

On the other hand, Tripett[99] has found that phosphetans themselves undergo hydrolysis and related reactions either to give an equilibration of geometrical isomers, a general lack of stereospecificity or a mixture of both. 1-Chloro-pentamethyl-phosphetan (83) undergoes nucleophilic substitution with predominant inversion of configuration and since the ring will occupy the apical/equatorial position in the intermediate phosphorane and the lone pair the other apical site, equatorial attack and departure has been suggested in this case.


R
Cl⁻
Cl
(85)
Cl
R
Cl
2
1
Cl
P
R
Cl
Cl
P
Cl
Cl
R
high
energy
Cl
P
Cl
R
Cl
Cl
P
R
Cl
other
isomer

SCHEME 24

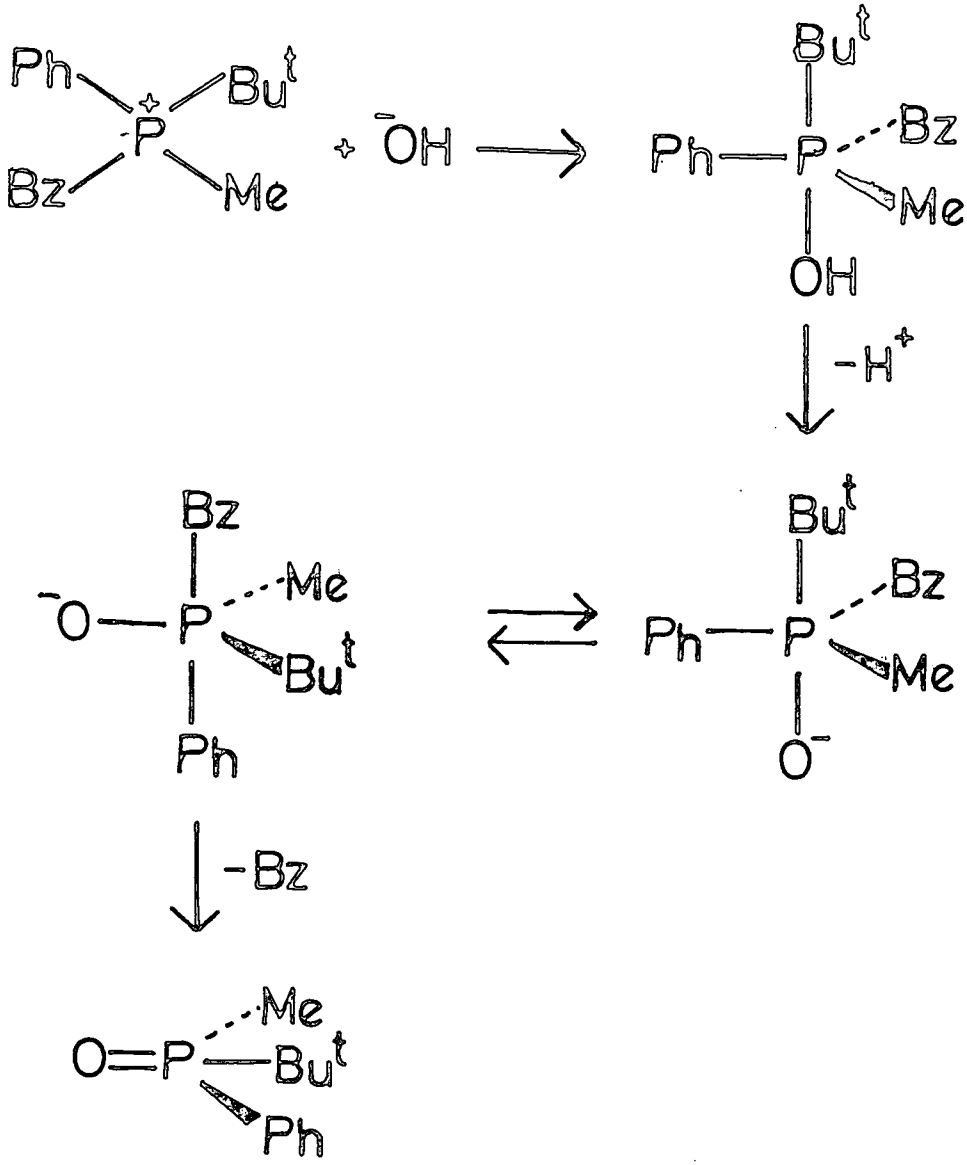
Smith[100] has noted that in the alkaline hydrolysis of phosphetans, that if X and Y (84) are of comparable electronegativity a loss of stereospecificity can occur through the pseudo-rotations shown.



Cremer[101] has confirmed this experimentally by observing an interconversion in solution between the isomers of a series of phosphetanium chlorides (85). Two possible pathways can be considered for this transformation. Firstly, the ring remains apical/equatorial throughout, and secondly the ring becomes diequatorial, as shown in scheme 24 (facing page).

The reaction was found to proceed via path 2, involving a diequatorial ring, by addition of aluminium trichloride which froze out the different isomers.

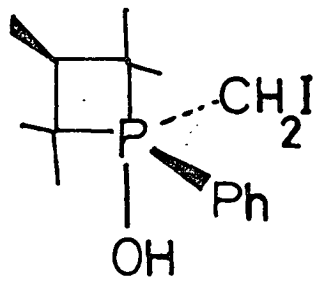
Exceptions to the above premises have been noted, however. Hudson and Brown[72] have observed retention of configuration in the hydrolysis of ~~ter~~t-butylmethylphenylbenzylphosphonium salts, presumably as the initial adduct formed will from steric considerations have


Ph
Bu^t
P
Bz
Me
$^-$OH
Bu^t
Ph
P
Bz
Me
OH
$-H^+$
Bz
$^-$O
P
Me
Bu^t
Ph
Bu^t
Ph
P
Bz
Me
O$^-$
$-$Bz
O=P
Me
Bu^t
Ph

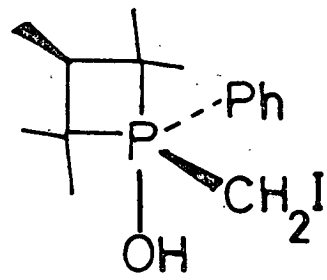
SCHEME 25

the ~~tert~~-butyl group apical (i.e. attack of hydroxyl from point opposite the most bulky group). Reaction as in scheme 25 (facing page) would then lead to retention, benzyl being the better leaving group.

Tripett et al[102] have observed phosphetans that react in alkaline hydrolyses with retention of configuration; cis-1-phenyl-1-iodomethyl-2,2,3,4,4-pentamethylphosphetanium salts gave only the cis-1-phenyl-2,2,3,4,4-pentamethylphospholan 1-oxides while the trans-isomer gave only trans-product. This was rationalised in terms of reaction via the phosphoranes (86) and (87) in the respective cases.



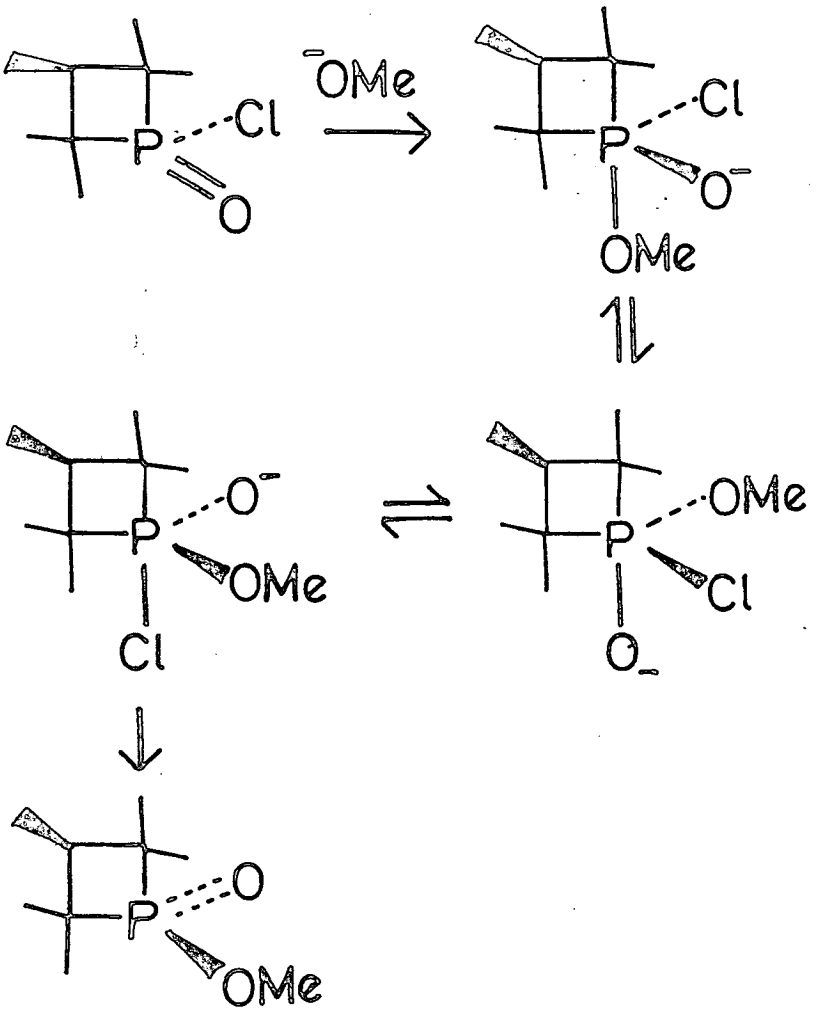
(86)



(87)

Departure (with ring cleavage) of the $-CMe_2$ groups must be accompanied by attack of the incipient carbanion on the iodomethyl group, with expulsion of the good leaving group $I^{(-)}$ and ring expansion. Furthermore, for stereochemistry to be retained this attack must be more rapid than any pseudo-rotation within the molecule.

Finally, Emsley et al[44] have noted that trans-1-chloro-pentamethylphosphetan oxide gave a mixture of cis and trans esters with aliphatic alcohols and phenol while other aryl alcohols gave only trans esters. This was shown to be a definite inversion process rather than an alkyl migration or any other mechanism.



SCHEME 26

For inversion to occur the reaction pathway outlined in scheme 26 (facing page) must be followed.

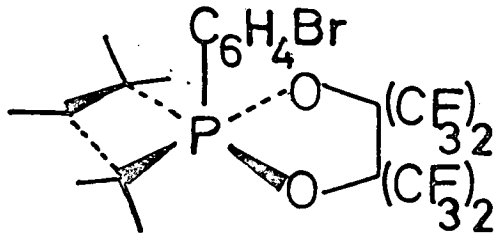
This does not occur more frequently as Cl is more apicophilic than $O^{(-)}$ and pseudo-rotation therefore usually proceeds as to place the Cl atom apical directly, and this leads to retention of configuration. Here there must therefore be some factor increasing the apicophilicity of $O^{(-)}$ against that of Cl.

The same general premises hold for other cyclic systems although each case has to be examined in the light of the other groups present. Mislow[103] concludes that when the displaced group is a poor leaving group and not markedly electronegative then retention will be observed for rings smaller than six-membered and inversion for larger rings. When the displaced group is a good leaving group with electronegativity comparable to that of the nucleophile then inversion may be noted in five-membered or larger rings, i.e. if both nucleophile and leaving groups are both significantly more electronegative than alkyl or aryl, apical attack leads to a phosphorane in which entering and leaving groups occupy the apical positions and relief of stereoelectronic strain more than compensates for the concomitant ring strain in placing the ring diequatorial. Furthermore, attack by intramolecular nucleophiles on phosphorus in acyclic systems also tends to lead to predominant retention of configuration since the intermediate phosphorane is incorporated in a small ring. The classic example of this must be the Wittig reaction and, indeed, McEwen et al[15] have observed just this effect.

Other Factors involved in Nucleophilic Substitution at Phosphorus

The premises outlined above are all based on pentacovalent intermediates or transition states having trigonal bipyramidal

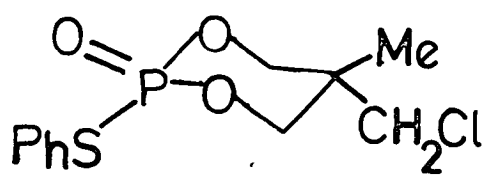
geometry. Tripett et al[24] have shown the spirobicyclic phosphorane (88) to have square pyramidal geometry, while Hudson et al[25] have



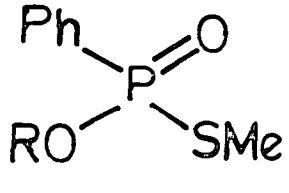
(88)

shown square pyramidal geometry for the intermediates or transition states in the alkaline hydrolysis of cyclic phosphonamidates. There is then the possibility of different stabilities arising than those on which the preceding discussion has been based.[74]

The product control exhibited by the methoxyl and hydroxyl groups in the hydrolysis of ethylene phosphate (65) and its O-methyl analogue (62) has already been discussed. Wadsworth Jr.[104] has shown that methanolysis of 5-chloromethyl-5-methyl-2-oxo-2-phenylthio-1,3,2-dioxaphosphorinan (89) under normal conditions proceeds with retention of configuration <u>via</u> a pseudo-rotating trigonal bipyramidal intermediate while when a better leaving group is available, e.g. $Cl^{(-)}$, inversion of configuration is noted. Similarly DeBruin and Johnson[105] have shown that methoxide ion selectively displaces thiomethyl with inversion at phosphorus in the methanolysis of O,5-dimethylphenyl phosphenothiolate (90).



(89)



(90)

Granoth et al[106] have extended the premise of product control by the relative apicophilicities of the nucleophile and leaving group as a chemical probe for determination of the relative apicophilicities of different groups by consideration of product ratios and structures, while Wilkinson et al[107] have shown that whereas most phosphono derivatives are hydrolysed more rapidly by hydroxide than the corresponding phosphoro derivative, the reverse situation holds for the S-alkyl analogues. The difference has been attributed to differences in the mechanism due to the labile P-S bond, S-alkylphosphonothioates hydrolysing with inversion of configuration while S-alkylphosphorothioates proceed with retention.

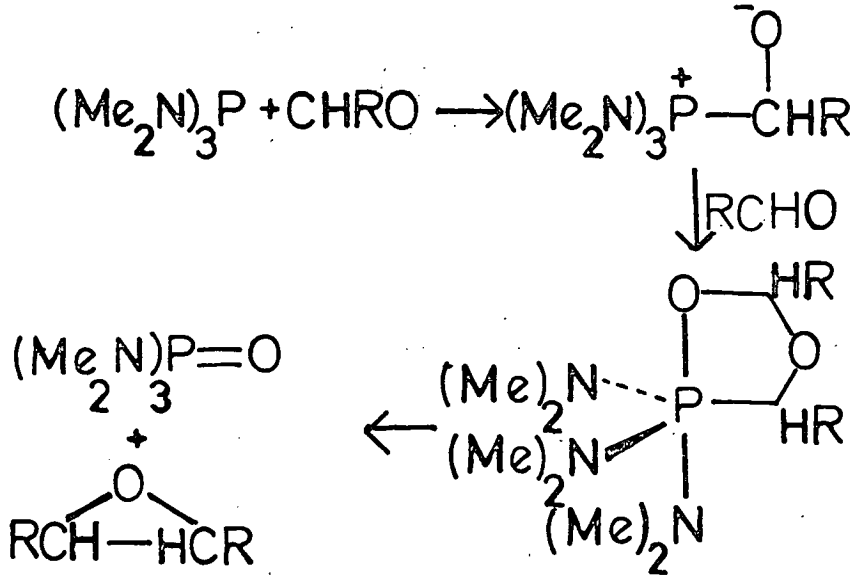
Finally, Cadogan et al[108] have observed a neighbouring group participation during alkaline hydrolysis of phosphonates of type (81), intramolecular participation of the oximate group giving a cyclic pentaco-ordinate intermediate, assisting the hydrolysis, while Hudson and Green[109] have similarly postulated formation, intramolecularly, of a cyclic five-membered phosphorane to explain the rapid release of phenol, in alkaline solution, from (2-aminoethyl)-diphenylphosphate.

(b) The Wittig Reaction

A vast amount of literature has appeared on the Wittig reaction. Here, however, the only concern is the effect of cyclic phosphorus moieties on the reaction. That the intermediate in the Wittig reaction is of a cyclic nature[15,16,17] has already been mentioned in the previous section on phosphetans, as has the similar reaction between phosphoramidates with aldehydes and ketones.[18]

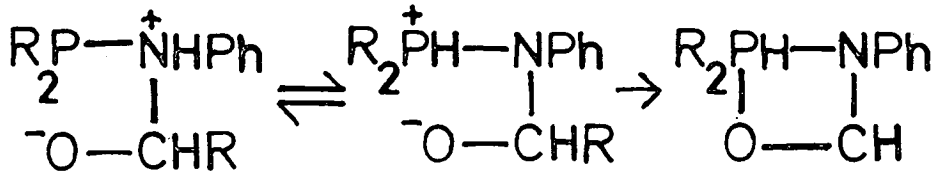
Mark[100] has observed that hexamethylphosphorus triamide reacts with two equivalents of aldehyde to give a phosphorane which

decomposes to give an epoxide as in scheme 27.



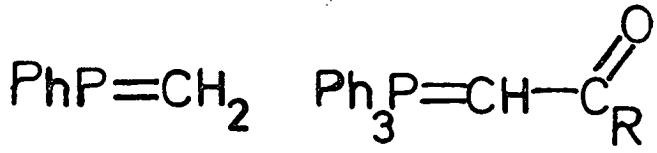
SCHEME 27

Similarly Hudson[111] has observed reaction of alkylphosphinous amides with ketones and aldehydes in a mechanism, similar to the Wittig reaction, proceeding *via* a four-membered cyclic transition state, and further observed that primary amine derivatives were more reactive than derivatives of secondary amines owing to the mobility of the amine proton in the former case[112] giving a neutral phosphorane, as shown below, while secondary amine derivatives gave the less stable charge separated phosphoranes of type (16).



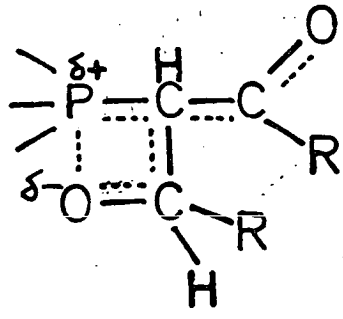
Since the Wittig reaction thus proceeds *via* cyclic transition states, in comparison to the arguments put forward for hydrolysis reactions, an acceleration of the Wittig (and similar) reactions

should be observed on using cyclic phosphorus reagents. Allen et al[113] have observed such an acceleration, the betaine intermediates derived from 5-phenyldibenzophosphole collapsing to products much more rapidly than those from acyclic triarylphosphines. Hudson et al[114] have similarly noted an acceleration in the Wittig reaction of acyclic ylides that are stabilised by the presence of a β-carbonyl group. Hence reaction of the standard ylide methylenetriphenylphosphorane (91) with benzaldehyde yields a betaine adduct which is stable and



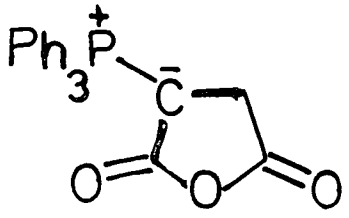
(91) (92)

isolable [115] while reaction of the stabilised ylide (92) gave a facile reaction where benzaldehyde disappeared simultaneously with appearance of phosphine oxide. The ease of the second reaction was attributed to the degree of conjugation which could exist in the transition species, viz. (93) which leads to easy formation of a stable α,β-unsaturated ketone.

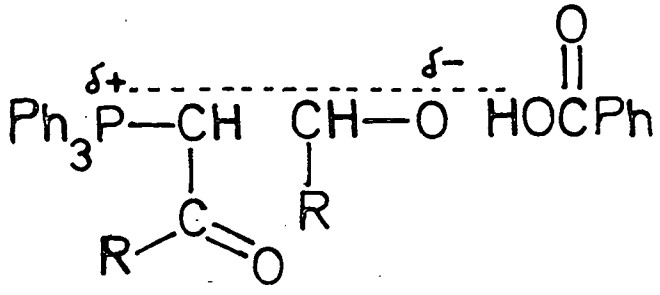


(93)

On the other hand the adduct between triphenyl phosphine and maleic anhydride (94) has been shown to resemble ylides with an α carbonyl group and yet no or poor yields of the expected olefins



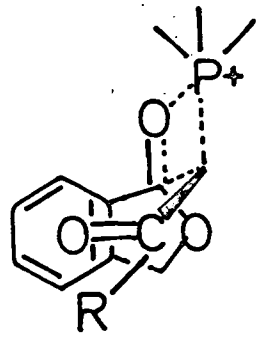
(94)



(95)

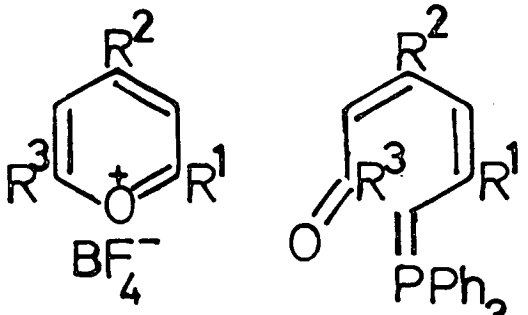
were obtained on reaction with aldehydes.[116] Furthermore, catalysis of the reaction, by benzoic acid, of carbethoxymethylene-triphenylphosphorane (92) and benzaldehyde has been shown to be reduced in chloroform or at elevated temperatures.[117] This has been postulated to suggest specific hydrogen bonding in the transition state (95).

Hudson et al[118] have observed a normal Wittig reaction between (92) and phthalic anhydride, where, however, the stereochemistry of the product depends on the nature of R in (92). When R = NR_2, OMe or OEt, the <u>cis</u> product was formed exclusively while R=Ph led to the <u>trans</u> isomer preferentially, and R=Me led only to <u>trans</u>. This was seen as due to the cyclic Wittig transition state forcing the COR group into a plane parallel to the phthalic anhydride ring as shown in (96). In this configuration the pπ electrons of R and C=O can interact strongly with the aromatic system and thus the observed



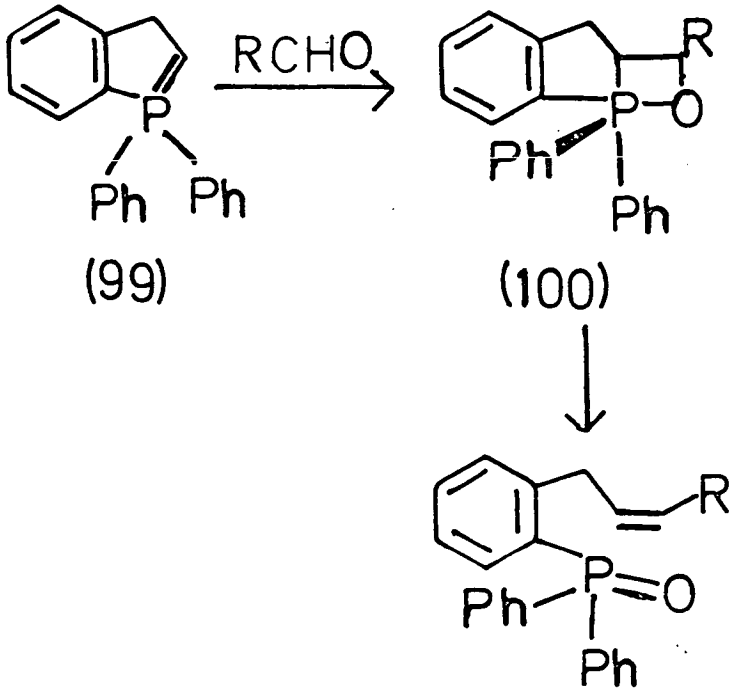
(96)

decrease in the cis/trans ratio with electron release capability to the C=O π orbital is expected. However similar reaction between the same ylides and carboxylic acid anhydrides was not observed.



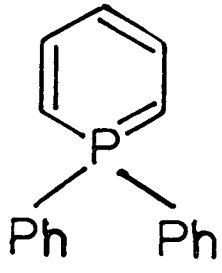
(97) (98)

Markl[119] has noted a neat method, involving the reaction of ylides (91) on pyrylium salts (97) to give the vinylogous phosphine-acyl-methylene (98), which can be made to undergo an intramolecular Wittig reaction to give the substituted aromatic compound. Cyclic compounds such as (99) underwent normal Wittig reactions[120] to give the bicyclic pentaco-ordinate intermediate (100) which decomposed with ring opening as shown. However, although the phosphabenzene

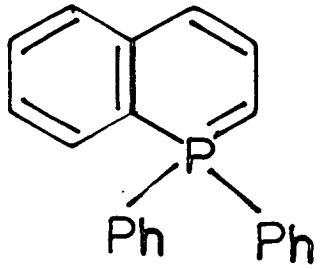


(99) (100)

and phosphanaphthalene (101 and 102) have the structural characteristics of a cyclic methylenephosphorane, Markl[120] has shown that they are stable in water and do not undergo Wittig reactions, even though the equilibrium

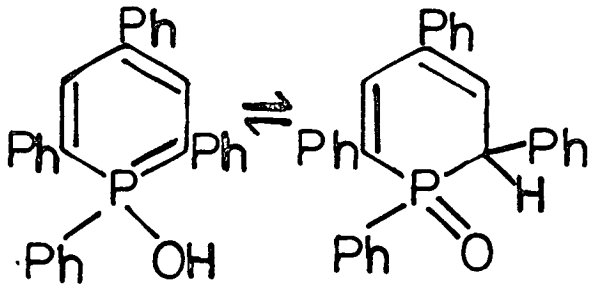


(101)



(102)

shown below has been observed even in weak bases and in water.[121]

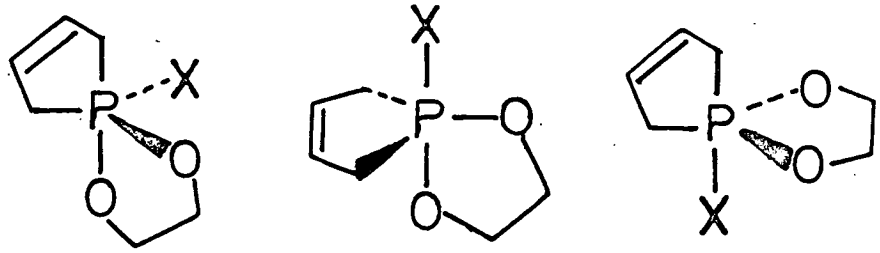


Kise[122] has reported a peculiar reaction between alkylidene-triphenylphosphoranes with lactones, the reaction proceeding via a triphenylphosphoniocarboxylate betaine which thermally decomposed to triphenylphosphine and lactones with the alkylidene groups of the phosphoranes introduced into the ring, rather than via a normal Wittig pathway.

(c) Other Reactions

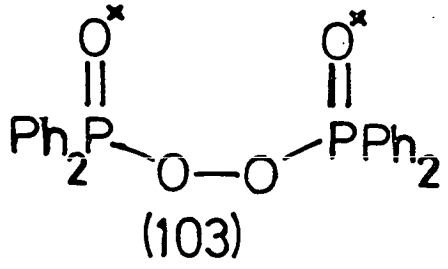
The reaction of various cyclic phosphines with diethyl peroxide[8] has already been mentioned, p.4, the reaction proceeding via phosphoranes with diequatorial ring placement. Denney et al[123] have extended this reaction to several other species. With 1,2-dioxane similar results to those with diethyl peroxide are obtained.

Here, however, diequatorial ring placement of the phospholene ring (5 and 6) is not so assured as the 1,2-dioxane cannot span the two apical positions and the reverse cycloaddition could occur from either of the three possibilities shown.

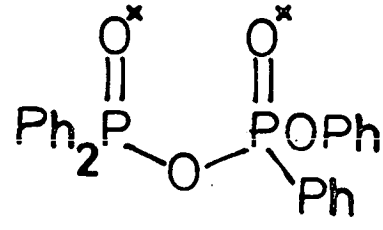


Reaction with trifluoromethyl hypofluorite or perfluorobutadiene gave intermediates which decomposed to difluorophosphoranes. However, reaction with tert-butyl perbenzoate, tert-or n-butyl hypochlorite or 3,4-bis(trifluoromethyl)-1,2,-dithietene gave the phosphine oxide or sulphide.

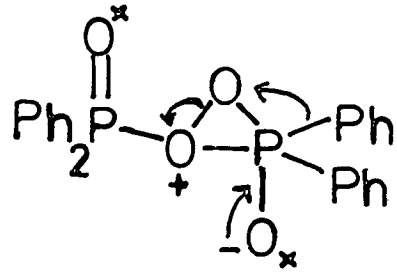
Hudson et al[124] have shown that the thermal rearrangement of bis-(diphenylphosphinyl)peroxide (103) labelled with ^{18}O in the phosphoryl oxygen positions to the unsymmetrical anhydride (104) proceeds with retention of ^{18}O in these positions. The proposed mechanism involves an intramolecular reaction and proceeds via (105),



(103)



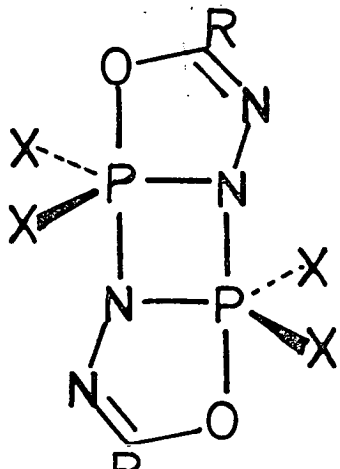
(104)



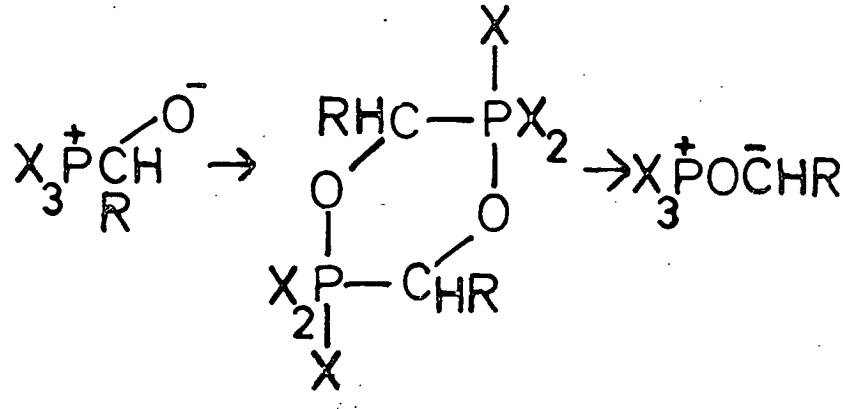
(105)

where there is extra stability due to the formation of the cyclic 3-membered phosphorane without inducing strain at the other phosphorus atom as in previously proposed mechanisms.[125] Similar three-membered cyclic phosphorus species have been postulated in several reactions.[126]

A novel demonstration of the possible relief of strain in making the transformation P(IV,V) → P(V,V) has been made by Schmidpeter and Luber.[127] O-aminophenole was found to react with chlorophosphoranes of type X_2PCl_3 in a cyclocondensation to give dimeric oxazaphospholines (106) containing two pentaco-ordinate phosphorus species, where the normally expected products of this type of reaction would normally be iminophosphines. A similar "diphosphorane" species (107) has been postulated by Ramirez et al.[128] in the reactions of tertiary phosphines with monocarbonyl compounds, when rearrangements from P-C-O adducts to P-O-C adducts are observed, as shown, although



(106)



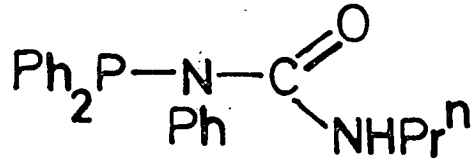
(107)

this is only observed when the negative charge on carbon can be accommodated by the presence of a suitable electron withdrawing substituent R, such as $-CF_3$.

Phosphorane formation has been reported also in trialkyl phosphite deoxygenations of various o-nitro-diaryl ethers and diaryl

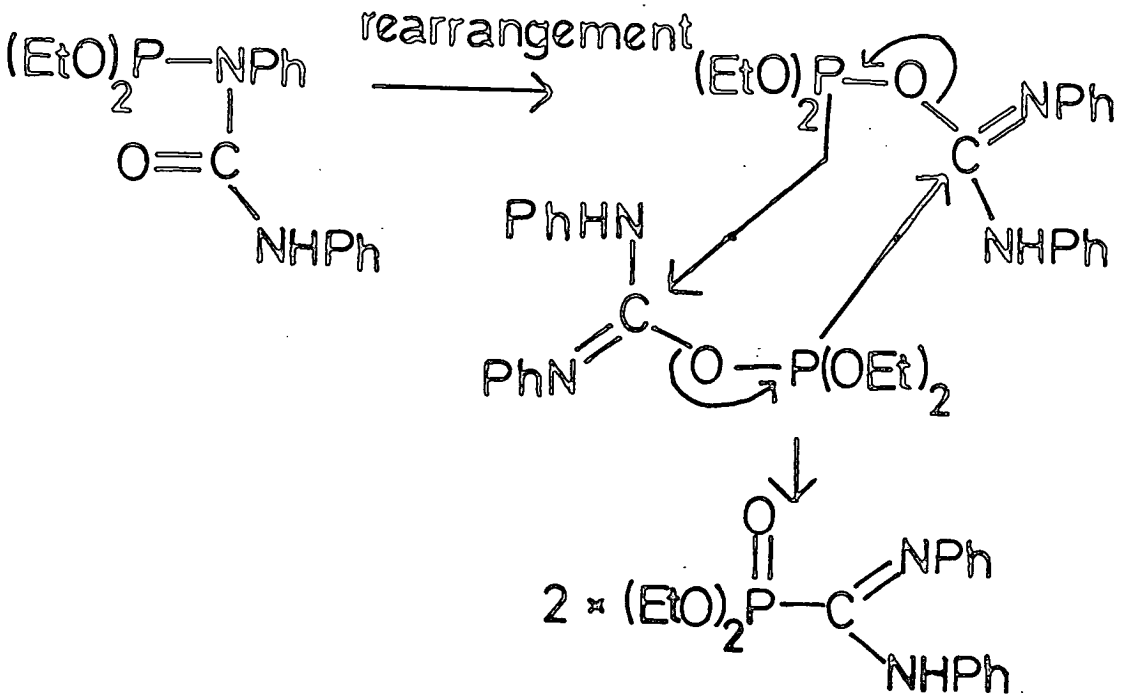
methanes[129] and have been isolated in some cases. In support, further, of the stability of bicyclic phosphoranes aryl-2-nitrophenyl sulphides have been shown to give oxythiazaphosphoranes with tervalent phosphorus reagents.[130] These phosphoranes isomerised readily to phosphoramidates except in the more stable bicyclic cases.

Finally, Hudson and Mancuso[131] have used the small ring effect, where an increase in rate is expected for cyclic phosphorus reagents in reactions involving nucleophilic attack at phosphorus, while a decrease in rate is to be expected for reactions involving nucleophilic attack by phosphorus, to attribute the rate determining step in the mechanism of the reaction of various phosphines with isocyanates. Different products are found in this reaction dependent on the structure of the reactants.[132] In general derivatives of secondary amines give mainly isocyanate dimer or trimer and some polymer, but derivatives of primary amines form no polymer and moreover the same product (108) was isolated from the reaction of phenylisocyanate with N-n-propyldiphenylphosphinous amide and of n-propylisocyanate with N-phenyl-diphenylphosphinous amide.



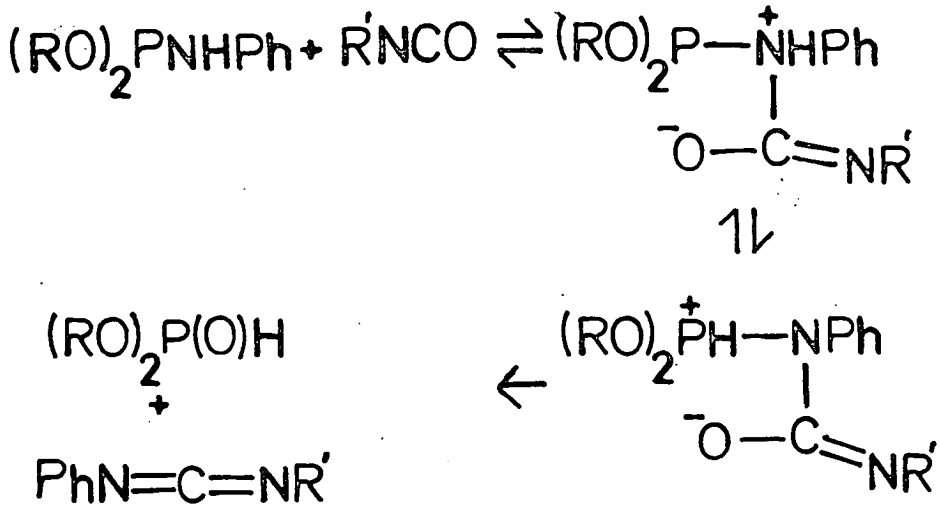
(108)

Clearly the amine proton of the primary amines greatly accelerates the reaction as in the reaction of alkylphosphinous amides with aldehydes and ketones mentioned previously,[112] which suggests a similar transition state. Phosphoramidates, however, react differently producing a carbodiimide as shown in


rearrangement
(EtO)2P—NPh
O=C
NHPh
(EtO)2P—O
C=NPh
NHPh
PhHN
C
PhN
O—P(OEt)2
O
2 × (EtO)2P—C
NPh
NHPh

SCHEME 29

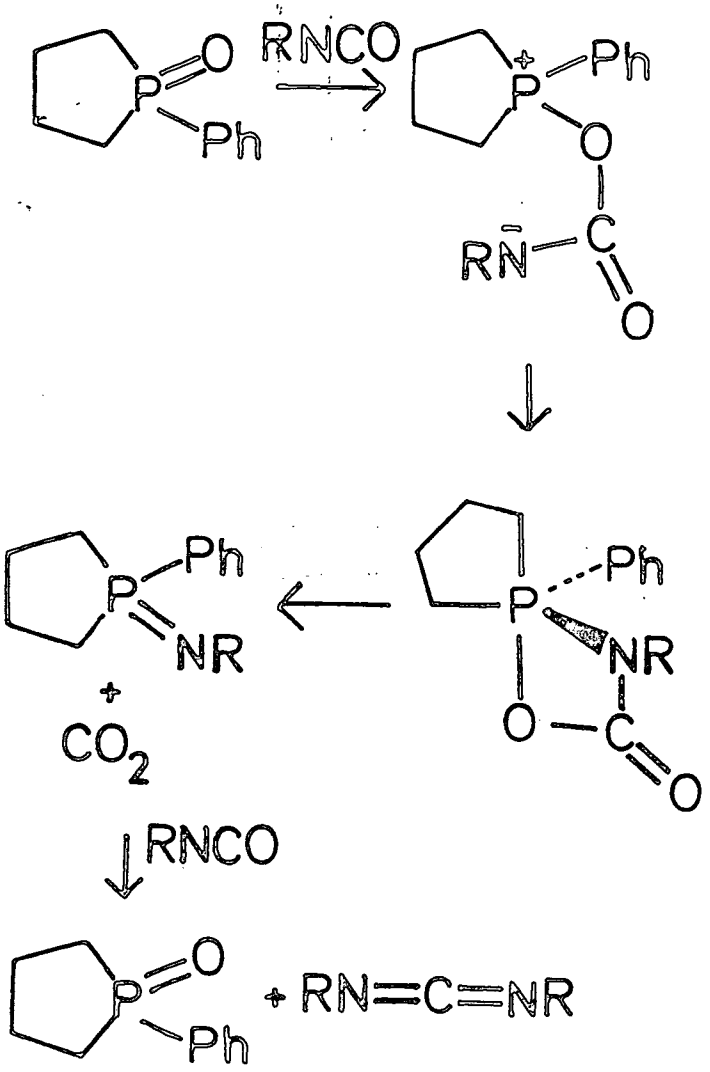
Scheme 28.



SCHEME 28

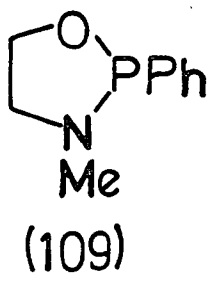
Hudson and Mancuso[131] have observed that cyclic N-dialkyl species are much more reactive to isocyanates than acyclic analogues, in agreement with a mechanism leading to an intermediate of type (16). In contrast the cyclic N-alkyl derivatives decrease in rate suggesting a rate-determining step involving quaternisation at phosphorus. Whatsmore they have observed a species similar to (108) in the reaction of aromatic isocyanates with N-arylphosphoramidites at lower temperatures.[133] At 100° a reaction takes place in which the species similar to (108) reacts as shown in Scheme 29, second order kinetics being observed, (facing page).

The acceleration noted by Greenhalgh and Hudson[18] for the reaction of isocyanates with cyclic phosphoramidites has already been noted. Reaction with N-methyl-P-phenyl-1,3,2-oxazaphospholan (109) is also accelerated. On the other hand, reaction with the P-methoxy analogue is no faster than in the acyclic analogue, the proposed transition state being (110), torsional strain increases

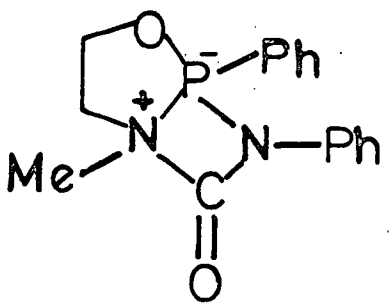


SCHEME 30

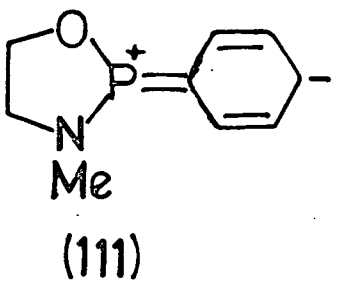
at the ring nitrogen offsetting ring strain release at phosphorus. The P-phenyl analogue (109) is proposed[134] to be more strained than the P-methoxy derivative in any case due to possible conjugation between phosphorus and the phenyl ring (111).



(109)



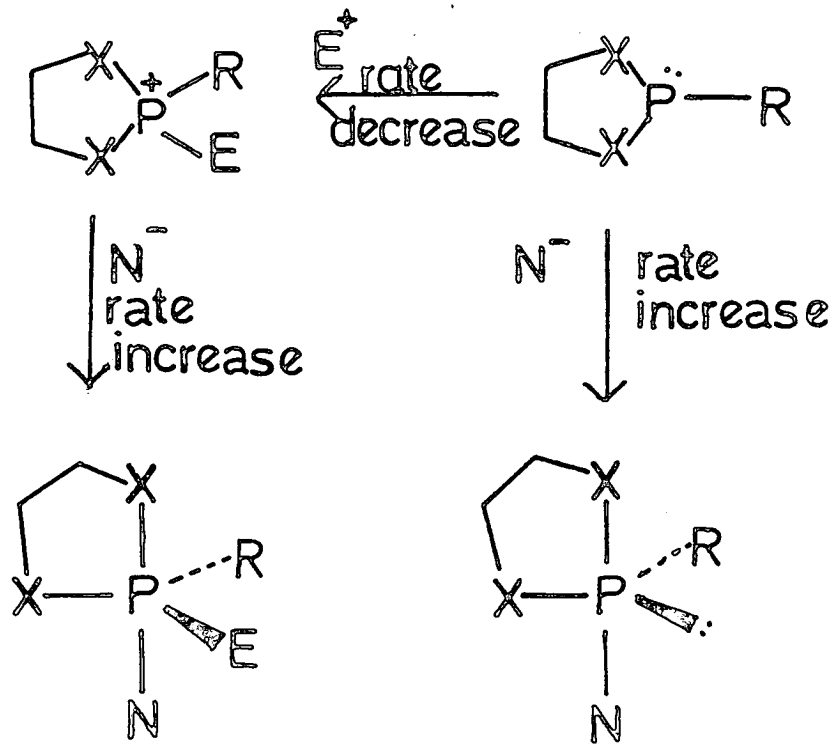
(110)



(111)

In a similar reaction phosphine oxides are known to catalyse the formation of carbodiimides from isocyanates,[135] phosphetan oxides having been shown to react remarkably smoothly, at least three orders of magnitude faster than acyclic phosphines. Phosphine imines have been shown to be intermediate in the reaction. Hudson and Brown[72] proposed the mechanism shown in Scheme 30 (facing page).

In support of this mechanism Aksnes and Froyen[136] have shown that there is an acceleration, compared to acyclic analogues, of some 10^3 in the rate for formation of the phosphinimine, in contrast to an acceleration of only 10 for subsequent reaction of the imine, in cyclic cases. Further they find an enhancement[137] of 23 for the cyclic species in the reaction of the N-acylphosphinimine to oxide and nitrile.



SCHEME 31

The Chemistry of Phosphorus Imines

Scott[140] has reviewed the chemistry of such compounds. As phosphorus nitrogen ylides they can undergo Wittig type reactions *via* the charge separated form (112).[141] They are also subject to acid catalysed and alkaline hydrolysis and several rearrangements have been noted.[140] In general, however, all the reactions of

$$(\equiv \overset{+}{P}-\bar{N}-)$$

(112)

these compounds are subject to, and can be explained by, the premises and constraints laid out in the preceding discussion.

The Small Ring Effect - In Conslusion

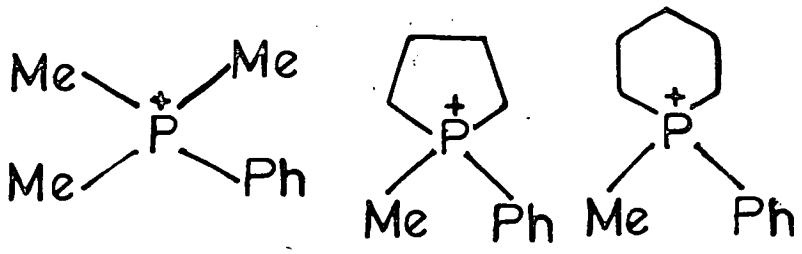
The small ring effect mentioned on p. 59, has its origins in Scheme 31 (facing page).

When phosphorus acts as a nucleophile the natural angle of phosphines and phosphites of *ca* 100° is increased to *ca* 109° and hence in a cyclic compound the ring strain should be increased[72] and the cyclic compound should be less reactive than its acyclic analogue as observed by Hudson[131] in the reaction of cyclic N-alkyl derivatives with isocyanates (see p. 59).

On the other hand nucleophilic attack at phosphorus to give a ten electron system should decrease the ring angle at phosphorus and the ring should be less strained and the cyclic species should be more reactive than acyclic analogues.

Similarly, nucleophilic attack at the positive phosphorus centre of a phosphonium salt to give a phosphorane will also lead

to a decrease in the bond angle and so this type of reaction would also be expected to show an increase in rate in cyclic species. The results obtained by Aksnes (see p. 39)[69] for the alkaline decomposition of species of types (113, 114 and 115) bear this out.



(113) (114) (115)

Further evidence comes from the observed acceleration of the Wittig reaction in small ring cases by Allen (p. 53),[113] the high reactivity of phosphetanium salts noted by Cremer and Chorvat (p. 43)[86] and the rate differences in a series of phosphonium salts by Cremer et al. (p. 39).[71]

It is obvious, therefore, that the reactions described in the preceding discussion are indicative of the power of the small ring effect when the magnitude of the accelerations and decelerations noted is considered.

The actual nature of the strain involved has been discussed in the light of the evidence available (see p. 3) and the apparent anomalies of "normal" rates of hydrolysis for some phosphetans and other species explained in terms of steric hindrance competing with the small ring effect (p. 42-44).

The effect small rings can have on the stereochemistry of the products has been discussed (p. 45) in terms of the relief of strain in a cyclic phosphorane giving added stability to the

intermediate involved allowing ligand isomerisations to take place, while noting that care should be taken in such considerations to make allowances for possible product control due to other groups.

In a final demonstration of the power of the small ring effect the work by Smith[138] on the reaction of 1-phenyl-3-methylphosphol-2-ene (4) and benzoyl chloride is of note. It is known[139] that hydrolyses of acyclic acylphosphonium salts proceed *via* nucleophilic attack at the carbonyl carbon. When, however, the phosphorus is constrained in a ring as here the rate of attack at phosphorus is enhanced such that the initial attack occurs at phosphorus. Here then, as observed, hydrolysis of the intermediate acylphospholenium salts proceeds to give a strain free phosphorane, with a highly apicophilic acyl group, which then decomposes by apical loss to give the phospholene oxide and an aldehyde, rather than giving a ring expanded product, and ring strain has *via* the small ring effect, changed the mechanism and products observed. This idea is supported by the observation[138] that acylphospholium and acylphosphetanium salts, where the rings are more highly strained than in the phospholene, hydrolyse to phosphoranes where some strain is still present and that these phosphoranes collapse with ring expansion.

More Recent Developments in Phosphorus Chemistry

Further support for the concept of phosphoranes as intermediates or transition species has been found more recently, and many more stable phosphorane species have been identified.

Ramirez et al[187] have established a "one flask" reaction in which aryl cyclic enediol phosphates are used to generate two different alchols into a diakyl(1-methylacetonyl)phosphate such as $(R^1O)(R^2O)P(O)OCH(CH_3)COCH_3$.

The differing product ratios were explained by intermediacy of P(V) and P(VI) species with isomerisational rotation and the relative stabilities of different ligands and P(V) species themselves giving the observed variations. The effective reaction being similar in mode to that proposed by Haake et al[188] where a more reactive species is generated by nucleophilic attack at phosphorus via:

$$Nu + P(O)X_3 \longrightarrow NuP(O)X_3 \longrightarrow \underset{\text{more reactive}}{P(O)NuX_2} + X$$

The differing apicophilicity of various ligands, ring strain and steric factors were all investigated by Trippett[189] in the substitution at phosphorus in cyclic and spiro 5-coordinate phosphoranes.

Rotational energy barriers were calculated and indicated that all three factors could be important and supported the idea of apical attack at phosphorus to form trigonal bipyramids which undergo permutational isomerisation if sufficiently long-lived and then apical loss of leaving group.

Permutational isomerisation was also noted in a large variety of phosphoranes of the form $(RO)_5P$.[190] Varying stabilities of the phosphoranes were found dependent on R, and in no case was any non-equivalency of any particular group of atoms established by variable temperature ^1H or ^{13}C N.m.r., indicating rapid interchange positionally of the ligands around phosphorus.

Further, Holmes and Dieters[191] have performed variable temperature N.m.r. observations on cyclic phosphoranes and discovered that the mode governing ligand exchange in the species discussed was that described by Berry (see p.11) rather than the Turnstile Process (p.12 and 13).

Other Phosphorane Reactions Observed

In a series of papers Cadogan et al[192,193] have generated several stable phosphoranes and in a further paper[194] demonstrated that the hydrolysis of benzoxazaphospholes in aqueous dioxan gave endocyclic cleavage of the P-O bond, which by all previous discussions would be preferentially apical, followed by loss of methanol, while low yields of some P-N cleavage products indicated some recyclisation and ring opening sequence.

Ramirez et al[195], also, have indicated the direct observation of an hydroxyphosphorane in equilibrium with its ester in solution, the ^{31}P signal of both species being observed at low temperatures in aprotic solvent.

Finally, Hudson and Woodcock[196] have determined the rates of reaction for a series of phosphylated amide oximes

in alkaline solution and noted that the reaction paths are strongly influenced by the substitution at phosphorus and the strength of the acid released, and further noted a rate differential of 10^7 in favour of cyclic analogues with rapid ring opening. These observations are explained by a complicated reaction mechanism involving phosphorane transition species with permutational isomerisation.

Further Reading

Two reviews of interest in relation to the topics discussed above are those by Trippett[197] and Smith[198].

PROGRAMME OF RESEARCH

The following programme of research was followed in an attempt to demonstrate the dependence of the rate of decomposition of iminophosphorus compounds on the ring strain present in the phosphorus moiety.

Programme

1. To synthesise a variety of iminophosphorus compounds containing phosphorus moieties
   (a) of different ring size,
   (b) of open-chain type,
   (c) containing different activating groups/atoms.
2. To thermolyse these compounds under standard conditions and to measure the rate of decomposition by monitoring the increase in concentration of 5-substituted benzofurazan - one of the decomposition products - by ^{1}H N.m.r. spectroscopy.
3. To investigate the decomposition by ^{31}P N.m.r. spectroscopy and to compare the results with those obtained in 2.
4. To attempt to isolate any intermediate which may be present in the reaction.

SYMBOLS AND ABBREVIATIONS

i.r.	infrared
ν	wavenumber
s	singlet
d	doublet
c	complex
J	coupling constant
m/e	mass to charge ratio
b.p.	boiling point
m.p.	melting point
N.m.r.	nuclear magnetic resonance
t.l.c.	thin layer chromatography
g.l.c.	gas liquid chromatography
cm^{-1}	wavenumber
U.V.	ultraviolet
t	triplet
q	quartet

Instrumentation and General Procedures

Infrared Spectroscopy: A Perkin-Elmer 157G spectrometer was used for all spectra. Liquid samples were examined as thin films, solids as nujol mulls, chloroform solutions or as a mix with potassium bromide pressed in a hydraulic press. A polystyrene film was used as reference at 1603 cm^{-1}.

Nuclear Magnetic Resonance Spectroscopy: ^{1}H spectra were obtained from an A.E.I. EM360 spectrometer at a frequency of 60 MHz, and at 100 MHz from a Varian H.A.100 spectrometer. ^{31}P spectra were obtained from a Varian X.L.100 fourier transform spectrometer. Samples were examined as solutions in deuterochloroform, carbon tetrachloride or in one instance deuterium oxide. Tetramethylsilane was used as internal reference. Kinetic samples were prepared somewhat differently, however, this technique being explained in section D of the following discussion.

Mass Spectroscopy: Mass spectra were obtained with an A.E.I. MS902 mass spectrometer.

Mass Spectroscopy/Gas Liquid Chromatography: These spectra were obtained from a VG Micromass 12 spectrometer coupled to a Pye 104 chromatograph using nitrogen as carrier gas

Gas Liquid Chromatography: A Pye 104 chromatograph was used with flame ionisation detector and 1.5m x 4mm packed columns of 2 or 5 per cent neopentylglycol succinate (N.P.G.S.) supported on 100-120 mesh celite using nitrogen as carrier gas.

Column Chromatography: Alumina used was Laporte Industries Ltd., grade H100-120 mesh. (Brockman activity 1-2).

Thin Layer Chromatography: Chromatograms were obtained using 0.25mm layers of alumina (Merck Aluminium Oxide G (type E)) on glass plates and developed under U.V. light or by the action of iodine vapour.

Elemental Analysis: Micro-analysis for carbon, nitrogen and hydrogen were performed by Mr. J. Grunbaum, University of Edinburgh using a Perkin-Elmer 240 elemental analyser.

Solvents and Reagents: Benzene and petrol (light petroleum ether b.p. 40-60°) were purified by distillation and stored over sodium. Ether (diethyl ether anaesthetic grade) was dried over sodium. Methylene chloride was distilled and stored over molecular sieve. Toluene was purified and dried by the method described in Vogel[142]. All other solvents and reagents were distilled or recrystallised and stored over molecular sieve where appropriate, except triethylamine which was distilled and dried over sodium hydroxide.

A. PREPARATION OF MISCELLANEOUS MATERIALS

1. AZIDES

(a) 4-Azido-3-nitrotoluene

4-Azido-3-nitrotoluene was prepared by a modification of the method described by Fitton and Smalley[143], by diazotising 4-amino-3-nitrotoluene in 5N hydrochloric acid and reacting the diazonium salt solution with sodium azide. The reaction mixture was extracted with ether, when column chromatography on alumina with ether as eluent gave the product as pale yellow needles (64%), m.p. 36° (lit[144], m.p. 36°).

I.r. $\nu_{max_{(cm^{-1})}}$: 2110 ($-N_3$), 1500 and 1530 ($-NO_2$)

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ: 7.9-7.1 (c, aromatic protons, 3H),
2.4 (s, methyl protons, 3H).

M.s. Found: parent ion m/e; 178

Calculated for $C_7H_6N_4O_2$: m/e; 178.

(b) 4-Azido-3-nitroanisole

4-Azido-3-nitroanisole was prepared as in (a) above while the temperature of the reaction mixture was kept between 0° and 5°. Column chromatography on alumina in petrol/ether (50:50 v/v) gave the product as yellow needles (54%), m.p. 74-76° (lit[145], 74°).

I.r. $\nu_{max_{(cm^{-1})}}$: 2110 ($-N_3$), 1500 and 1535 ($-NO_2$), 1210 (c-o).

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ: 7.5-6.5 (c, aromatic protons, 3H),
3.9 (s, methoxyl protons, 3H).

M.s. Found: parent ion m/e; 194

Calculated for $C_7H_6N_4O_3$: m/e; 194.

(c) 2-Azido-pyridine-1-oxide

(i) 2-Amino-pyridine-1-oxide was isolated as its hydrochloride by the reaction of 2-amino-pyridine with m-chloro-perbenzoic acid as in the method of Pentimalli[146]. The product (80%) had m.p. 158-159° (lit[144], 158-160°).

I.r. $\nu_{max_{(cm^{-1})}}$ 3300-3100 and 2480 ($-\overset{+}{N}H_3$, broad); 1310 (N-oxide)

N.m.r. (^1H, 60 MHz, D_2O) δ: 8.1-7.5 (c,2H), 7.2-6.6 (c,2H), 4.8 (s, 3H,$-\overset{+}{N}H_3$)

M.s. Found: parent ion m/e; 110

Calculated for $C_5H_7N_2OCl$: m/e; 146.

(Parent ion found is 146, less HCl, to give the free amine).

(ii) The hydrochloride thus prepared was taken up in 10% hydrochloric acid, diazotised, and reacted with sodium azide by the method of Abramovitch and Cue[147]. Extraction with methylene chloride and recrystallisation from petrol/benzene (1:1 v/v) gave the required azide (40%), m.p. 83-85° dec. (lit[147], 83° dec.).

I.r. $\nu_{max_{(cm^{-1})}}$ KBr: 2150, 2110 ($-N_3$), 1250 (N-oxide)

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ: 8.2 (d. of d., H_6, $J_{5,6}$ = 1 Hz), 7.15 (c, 3H, H_3, H_4, H_5).

M.s. Found: parent ion m/e; 136

Calculated for $C_5H_5N_4O$: m/e; 136.

2. 1,4-Diphenylbuta-1,3-diene

1,4-Diphenylbuta-1,3-diene was prepared by the method of Corson[148] using the condensation of phenylacetic acid with cinnamaldehyde in the presence of litharge with acetic anhydride as solvent. The product (21%) was obtained as white crystals, m.p. 152-153° (lit[148], 152-153°).

I.r. $\nu_{max_{(cm^{-1})}}$: 1610, 1600, 1520 (unsaturated and aromatic C-H)

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ: 7.8-7.0δ (c, 11H), 7.0-6.7δ (m, 3H).

M.s. Found: parent ion m/e; 206

Calculated for $C_{16}H_{14}$: m/e; 206.

3. Benzofuroxans

(a) 5-Methoxybenzofuroxan

5-Methoxybenzofuroxan was prepared by the method of Green and Rowe[149]. 4-Amino-3-nitroanisole (10g) was suspended in 150 ml of saturated alcoholic sodium hydroxide solution. To this, was added with cooling, commercial aqueous sodium hypochlorite until the red colour disappeared. The fluffy yellow precipitate was washed well with cold water and recrystallised from ethanol (61%), m.p. 115-118° (lit[150], 118°).

I.r. $\nu_{max_{(cm^{-1})}}$: 1640 and 1625 (-C=N-), 1600 and 1590 (C=C), 1210 (N-oxide), 1015 (C-O)

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ: 7.5-6.5 (c, 3H, conjugated olefinic protons), 3.9 (s, 3H, methoxyl protons)

M.s. Found: parent ion m/e; 166

Calculated for $C_7H_6N_2O_3$: m/e; 166.

5-Methylbenzofuroxan

5-Methylbenzofuroxan was prepared from 4-amino-3-nitrotoluene as in (a) above. The product (89%) was obtained as yellow needles, m.p. 96-97° (lit[150], 98°).

I.r. $\nu_{max_{(cm^{-1})}}$: 1620 and 1600 (C=N), 1280 (N-oxide)

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ: 7.5-6.9 (c, 3H, conjugated olefinic protons), 2.4 (s, 3H, methyl protons)

M.s. Found: parent ion m/e; 150

Calculated for $C_7H_6N_2O_2$: m/e; 150.

4. Benzofurazans

(a) 5-Methoxybenzofurazan

5-Methoxybenzofurazan was prepared from the benzofuroxan, prepared in 3(a) above, by the method of Zincke and Schwarz[151]. The product was obtained as a fluffy off-white solid (25%), m.p. 97-99° (lit[152], 99°) from light petrol (40-60).

I.r. $\nu_{max_{(cm^{-1})}}$: 1650 (C=N), 1020 (C-O)

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ: 7.8-6.8 (c, 3H, conjugated olefinic protons), 3.9 (s, 3H, methoxyl protons).

M.s. Found: parent ion m/e; 150

Calculated for $C_7H_6N_2O_2$: m/e; 150

Analysis Found: C,55.8; H,3.9; N,18.4%

Calculated for $C_7H_6N_2O_2$: C,56.05; H,4.0; N, 18.7%.

(b) 5-Methylbenzofurazan

(i) 5-Methylbenzofurazan was prepared as in 4(a) above, from 5-methylbenzofuroxan. The product was recrystallised from light petrol (40-60).

(ii) 5-Methylbenzofuroxan (0.45g, 0.003 mol) was refluxed in benzene, under nitrogen, for 2 hours in the presence of triethyl phosphite (0.5g, 0.003 mol). The reaction mixture was then chromatographed on alumina in ether, and the product sublimed to give a white crystalline solid, m.p. 36-37° (lit[152], 37°).

I.r. $\nu_{max_{(cm^{-1})}}$ 1640 (C=N)

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ: 7.8-7.2 (c, 3H, conjugated olefinic protons), 2.5 (s, 3H, methyl protons).

M.s. Found: parent ion m/e; 134

Calculated for $C_7H_6N_2O$: m/e; 134.

5. N,N'-Diphenylethylenediamine

N,N'-Diphenylethylenediamine was prepared by a modification of the method described in Vogel[142]. A mixture of 1,2-dichloroethane (20g, 0.2 mol) and an 8 molar excess of aniline (to repress formation of tertiary amine) was heated under reflux for 12 hours. The reaction mixture was then made alkaline, treated with hot water, extracted with ether, the ether removed and excess aniline removed by distillation. The residue was extracted with ether, and on removal of solvent, the product (60%) was recrystallised from dilute alcohol to give pale brown flakes, m.p. 64-66° (lit[153], 66°).

I.r. $\nu_{max_{(cm^{-1})}}$: 3400 (secondary NH), 1600 (aromatic C=C)

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ: 7.3-6.5 (c, 10H, aromatic protons), 3.35 (s, 4H, aliphatic protons), 3.3 (s, 2H, NH protons).

6. Diphenyl Disulphide

Thiophenol (13.5g, 0.12 mol) was placed, in ether, in a 500 ml, 3-necked, round bottomed flask fitted with condenser and dropping funnel. Sodium hypochlorite was then run into the mixture with stirring, a precipitate being immediately evident. After stirring for 15 mn. zinc dust was added to the reaction, the solution turning from yellow to green/blue. The reaction mixture was then stirred for a further 15-30 mn. and filtered, to give two layers, which were separated, and the yellow ethereal layer evaporated giving a white solid, which was recrystallised from ethanol, yielding diphenyl disulphide (78%) as white needles, m.p. 60-61° (lit[154], 60-61°).

I.r. $\nu_{max_{(cm^{-1})}}$: 1580 (aromatic C=C), 685 (C-S)

N.m.r. (^{1}H, 60 MHz, $CDCl_3$) δ: 7.7-7.2 (c, aromatic protons)

M.s. Found: parent ion m/e; 218

Calculated for $C_{12}H_{10}S_2$: m/e; 218.

7. Cupric Stearate

Stearic acid (20g) was reacted with sodium hydroxide (M/2, 125 ml) on a steam bath for 12 hours. The resulting clear solution was filtered through several layers of gauze to remove unreacted acid. The soap was then dissolved in about 1ℓ. of warm water, this solution then being poured into an excess of a 1% solution of cupric chloride, with vigorous stirring. The precipitate was washed by decantation, then dried in an air bath at 115-120° for a further 12 hours. The salt (85%) was then powdered and stored, m.p. 118-123° (lit[153], 125°).

M.s. Found: parent ion m/e; 284

Calculated for $Cu(C_{18}H_{35}O_2)_2$: m/e; 630.

(No Cu compound has ever been observed to give a parent ion on the departmental spectrometer. Stearic acid, mass 284, melts at 70.1°[153] so appearance of peak at 284 shows product to be required stearate).

B. PREPARATION OF TERTIARY PHOSPHORUS COMPOUNDS

1. 1,2,5-Triphenylphosphole

1,2,5-Triphenylphosphole was prepared by the modification of the method of Campbell et al[155] used by R.J. Scott[170]. The product (22-30%) was obtained as yellow fluorescent needles, m.p. 187-189° (lit[155], 187-189°).

I.r. $\nu_{max(cm^{-1})}$: 1590, 1570 (aromatic C=C)

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ: 7.8-7.1 (c, aromatic and phosphole ring protons)

M.s. Found: parent ion m/e; 312

Calculated for $C_{22}H_{17}P$: m/e; 312.

2. 1-Methyl-2,5-diphenylphosphole

The method used was that of Braye[156], by the reaction of potassium on 1,2,5-triphenylphosphole in refluxing dioxan, under nitrogen, for 70 hours, followed by addition of methyl iodide on cooling. After stirring for 5 hours, the reaction mixture was poured onto ice. Acetic acid and methylene chloride were then added, the organic layer separated and dried over magnesium sulphate. Elution with carbon tetrachloride down a silica gel column gave a yellow powder, m.p. 107-110° (lit[156], 110-111°) which was not further purified.

I.r. $\nu_{max(cm^{-1})}$: 2250 ((P)-C-H); 1595 and 1575 (aromatic C=C), 900 (P-Me)

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ: 7.7-7.0 (m, 12H, aromatic and phosphole ring protons), 1.4 (s, 3H, methyl protons)

M.s. Found: parent ion m/e; 250

Calculated for $C_{17}H_{15}P$: m/e; 250.

3. 2-Chloro-1,3,2-dioxaphospholan

A mixture of phosphorus trichloride (55 ml, 0.68 mol) in dry methylene chloride was introduced into a round bottomed flask fitted with stirrer, dropping funnel and condenser fitted with a calcium chloride guard tube. Ethylene glycol (38.7 ml) was then added dropwise so that the mixture boiled gently. When gas evolution had ceased, the solvent was removed and the residue distilled at the water pump, under nitrogen, to give 2-chloro-1,3,2-dioxaphospholan (69%), b.p. 62-64° at 30 mm. Hg. (lit[157], 65-66° at 42 mm. Hg.).

I.r. $\nu_{max_{(cm^{-1})}}$: 1210 (P-O-C), 1000 (C-O), 930 (ring)

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ: 5.0-3.8 (b, 4H).

4. 2-Chloro-1,3,2-dioxaphosphorinan

2-Chloro-1,3,2-dioxaphosphorinan was prepared from phosphorus trichloride (55 ml) and propane-1,3-diol (54.6g, 0.72 mol) as in (3) above, distillation giving the product as a clear oil, b.p. 63-66° at 12 mm. Hg. (46%) (lit[158], 54-55° at 9 mm.).

I.r. $\nu_{max_{(cm^{-1})}}$: 1060 (C-O); 935 (ring); 1240 (P-O-C)

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ: 5.0-3.2 (c, 4H, protons on C_4 and C_6), 2.9-1.4 (c, 2H, protons on C_5).

5. N-Dimethyl-1,3,2-dioxaphospholan

Dimethylamine gas was passed through a solution, under nitrogen, of 2-chloro-1,3,2-dioxaphospholan in benzene until the reaction was complete. The reaction mixture was then filtered and distilled, under nitrogen, at the water pump.

Benzene distilled first, b.p. 18-20° at 27 mm. Hg. This was followed by N-Dimethyl-1,3,2-dioxaphospholan (62.5%), b.p. 60-63° at

17 mm. Hg. (lit[159], 62° at 11 mm. Hg.).

I.r. $\nu_{max_{(cm^{-1})}}$: 1010 (C-O); 925 (ring), 685 (P-N)

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ: 4.3-3.7 (c, 4H, ring protons), 2.65 and 2.5 (d, 6H, N-methyl protons, J_{PH} = 9 Hz).

$\delta^{31}P$; +141(lit[160], +140)

6. N-Dimethyl-1,3,2-dioxaphosphorinan

2-Chloro-1,3,2-dioxaphosphorinan (6.0g, 0.043 mol) was reacted with dimethylamine as in (5) above. Distillation at the vacuum pump gave a clear liquid (93%), b.p. 44-46° at 3 mm. Hg.

I.r. $\nu_{max_{(cm^{-1})}}$: 1060 (C-O); 930 (ring); 690 (P-N)

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ: 4.3-3.9 (c, 4H, protons on C_4 and C_6), 2.7 and 2.55 (d, 6H, N-methyl protons, J_{PH} = 9 Hz), 2.2-1.2 (c, 2H, protons on C_5)

$\delta^{31}P$; +144 (lit[160], +143.4).

7. 2-Phenyl-1,3,2-dioxaphospholan

Dichlorophenylphosphine (9.0g, 0.05 mol) was added dropwise to an ice-cooled solution of ethylene glycol (3.1g, 0.05 mol) and triethylamine (10.1g, 0.1 mol) in benzene (100 ml) after the method of Mukaiyama et al[161]. After heating at reflux for 1 hr., the reaction mixture was filtered, the benzene removed in vacuo and the residue distilled from dry glass wool, under reduced pressure, to give a clear oil (65%), b.p. 64-65° at 0.15 mm. Hg. (lit[161], 80° at 0.8 mm).

I.r. $\nu_{max_{(cm^{-1})}}$: 1590 (aromatic C=C); 1435 (P-Ph); 915 (ring)

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ: 7.4 (c, 5H, aromatic protons), 4.2-3.7 (c, 4H, ring protons).

8. 2-Methoxy-1,3,2-dioxaphospholan

2-Chloro-1,3,2-dioxaphospholan (10g, 0.08 mol) was placed in benzene solution with triethylamine (8.1g, 0.08 mol). Methanol (3.8g, 0.08 mol) was then added dropwise, with stirring, under nitrogen. On completion of the addition, the reaction mixture was filtered, the benzene removed and the residue distilled to give the product as a clear mobile oil (85%), b.p. 20° at 0.2 mm (lit[162], 44.5° at 15 mm).

I.r. $\nu_{max_{(cm^{-1})}}$: 1210 (P-O-Me); 1040 ((P)-O-C); 925 (ring); 730 (P-O-(C))

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ: 4.3-3.7 (c, 4H, ring protons), 3.5 and 3.3 (d, 3H, P-methoxyl protons, J_{PH} = 11 Hz).

9. 2-Phenyl-1,3,2-dioxaphosphorinan

A solution of dichlorophenylphosphine (17-9g, 0.1 mol) in benzene (100 ml) was added dropwise to a stirred solution of carefully dried propane-1,3-diol (7.6g, 0.1 mol) and freshly distilled triethylamine (20.2g, 0.2 mol) in benzene (100 ml) as in (7) above. After the addition the reaction mixture was heated at 45° for 45 mn., filtered and cooled in the fridge. Further triethylamine hydrochloride was then removed by filtration, the benzene removed in vacuo and the residue distilled to give a clear, transparent oil (60%), b.p. 106-8° at 0.8 mm. Hg (lit[163], 96-98° at 0.3 mm.)

I.r. $\nu_{max_{(cm^{-1})}}$: 1435 and 1000 (P-Ph), 930 (ring), 1050 (P-O-alkyl)

N.m.r. (^1H, 60 MHx, $CDCl_3$) δ : 7.7-7.2 (s, 5H, P-Ph protons), 4.3-3.6 (m, 4H, $^-OCH_2^-$), 2.9-1.1 (m, 2H, $-CH_2^-$)

$\delta^{31}P$; 153.17.

10. 1-Phenylphospholan

1-Phenylphospholan was prepared by the method of Issleib and Hauslet[164] using the action of dichlorophenylphosphine on the di-Grignard of 1,4-dibromobutane. The di-Grignard was prepared in the usual way and then transferred to a 250 ml dropping funnel attached to a 3-litre 3-necked flask fitted with a mechanical stirrer and a further dropping funnel. The flask was flushed with nitrogen and charged with about 1.5 l of ether. Dichlorophenylphosphine was then made up in ether, to the same volume as the di-Grignard, in the second funnel and the two solutions dripped into the flask at the same rate, while stirring vigorously. The solution meanwhile was cooled to 0° in an ice/acetone bath. After the addition the reaction mixture was stirred for 1 hour at 0° and then 1 hr at room temperature before being cooled in ice and treated with diethylamine (2x100 ml). The reaction mixture was then filtered rapidly at the water pump (in a vigorous draught), the lower boiling fractions removed and the residue distilled under nitrogen, at the vacuum pump giving a clear mobile oil (25%), b.p. 88-90° at 0.9 mm. Hg. (lit[164], 97° at 3 mm.)

I.r. $\nu_{max_{(cm^{-1})}}$: 1435 and 1010 (P-Ph); 920 (ring)

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ : 7.5-7.2 (c, 5H, aromatic protons), 2.2-1.6 (c, 8H, ring protons).

$\delta^{31}P$; -15.76.

11. Diethylphenylphosphine

Diethylphenylphosphine was prepared as in (10) above using ethyl bromide (69.33g, 0.168 mol) and dichlorophenylphosphine (45g, 0.25 mol). Distillation (twice) gave a clear oil, (35.7%), b.p. 58-62°

at 0.25 mm. Hg. (lit[165], 60-65 at 2 mm.)

I.r. $\nu_{max_{(cm^{-1})}}$: 1433 and 1025 (P-Ph); 1235 (P-Et)

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ : 7.7-7.1 (c, 5H, aromatic protons), 1.9-1.3 (d. of t., P-CH_2 protons), 1.3-0.6 (d. of q., -CH_3 protons) J_{PH} = (P-C-CH_3) = 8 Hz.

$\delta^{31}P$; -15.57.

12. 1-Phenylphosphorinan

1-Phenylphosphorinan was prepared from 1,5-dibromopentane (53.3g, 0.23 mol) and dichlorophenylphosphine (41.53g, 0.23 mol) as in 10 above. Distillation (twice) gave a clear oil (31%), b.p. 85-88° at 0.3 mm. Hg. (lit[166], 75-85° at 0.5-1 mm.).

I.r. $\nu_{max_{(cm^{-1})}}$: 1435 and 1010 (P-Ph), 915 (ring).

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ : 8.3-7.3 (c, 5H, aromatic protons), 3.7-2.9 (m, 4H, P-CH_2), 1.5-1.0 (c, 6H, ring protons).

13. Phenylphosphinic Acid

Note: Although formally recognised here as a tertiary phosphorus compound, viz: $PhP(OH)_2$, phenylphosphinic acid exists 99% as PhP(O)(H)OH.

Dichlorophenylphosphine (167.8g, 0.94 mol) was dripped, with stirring into water (distilled, 250 ml). The water was then removed by distillation from a water bath. On cooling the greeny yellow residue gave white leafs of phenylphosphinic acid (40%), m.p. 83-6° (lit[153], 83-6°).

I.r. $\nu_{max_{(cm^{-1})}}$; 2380 (P-H); 1440 (P-Ph); 3000-2500, 2400-2200, 1750-1600, and 970 ($-P\lesssim^{O}_{OH}$ [167]).

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ : 10.7 (s, OH), 7.9-7.0 (c, P-Ph), 12.2 and 2.9 (d, P-H, J_{PH} = 564 Hz).

M.s. Found: parent ion m/e; 142

Calculated for $C_6H_7O_2P$: m/e; 142

$\delta^{31}P$: 19.45±0.6 ppm.

14. Dibromophenylphosphine

Phosphorus tribromide (123.7g, 0.35 mol) was allowed to react with phenylphosphinic acid after the method of Quin et al[168]. No external cooling was required and after 24 hr. with agitation two layers had formed. The lower layer was separated and distilled through an 8 mm. Vigreux column, under nitrogen, at the water pump.

Excess phosphorus tribromide was recovered first, b.p. 60° at 15 mm. Hg. Dibromophenylphosphine (83%) then distilled, b.p. 136-138° at 15 mm. Hg. (lit[169], 121-123° at 11 mm.).

I.r. $\nu_{max_{(cm^{-1})}}$: 1435 and 1000 (P-Ph), 690 (P-BR).

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ: 8.1-7.7 (c, 2H, ortho protons), 7.6-7.3 (c, 3H, meta and para protons).

$\delta^{31}P$: +151.29.

15. Phenylphosphine

Phenylphosphine was firstly prepared by the method of Freedmann and Doak[170] using the reaction of lithium aluminium hydride on dichlorophenylphosphine. However, for the preparation of sizeable quantities this led to unwieldy volumes of solution.

In order to avoid exposure to such volumes the method of Mann and Millar[171] was used where dichlorophenylphosphine was allowed to react with an excess of ethanol, and the resulting solution reduced in volume at the vacuum pump before the reaction mixture was disproportionated by heating, when phenylphosphine (35.2g) distilled over, b.p. 80-82° at 30 mm. Hg., the water pump being connected via two charcoal towers.

I.r. $\nu_{max_{(cm^{-1})}}$: 2280 (P-H), 1480 and 1035 (P-Ph)

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ : 7.7-7.5 (c, 2H, σ-hydrogens to P on benzene ring), 7.5-7.2 (c, 3H, ring protons), 5.7 and 2.3 (d, 2H, P-H protons, J_{PH} = 204 Hz)

$\delta^{31}P$: -122.4

N.B. All operations were carried out in a vigorous draught. Phenylphosphine ignites spontaneously in air at its boiling point. Storage in benzene solution helps to prevent air oxidation.

16. 3-Hydroxypropylphenylphosphine

3-Hydroxypropylphenylphosphine was prepared by the method of Korshak et al.[172] Allyl alcohol (16.8g, 0.29 ml) was dripped onto phenylphosphine (35.2g, 0.32 mol), under nitrogen, at 40°. The reaction mixture was then heated to 100° and kept there for 40 hr. The mixture was then distilled to give 10g (21%) of a clear oil, b.p. 106-8° at 1 mm. Hg. (lit[172] 107-108° at 3 mm).

I.r. $\nu_{max_{(cm^{-1})}}$: 3340 (-OH), 2280 (P-H), 1435 and 1020 (P-Ph)

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ : 11.5 and 4.2 (d, 1H, P-H proton), 7.8-7.1 (c, 5H, ring protons), 4.2 (s, 1H, hydroxyl proton),

3.7-3.4 (c, 2H, $-OCH_2-$protons), 2.3-1.5 (c, 4H, $-CH_2-$protons) $\delta^{31}P$: +4.83 ppm.

17. 1-Phenyl-2-oxaphospholan

3-Hydroxypropylphenylphosphine (6.7g, 0.04 mol) was allowed to react with diphenyl disulphide (8.7g, 0.04 mol) in benzene at 22° for 24 hr. as in the method of Grayson and Farley[173]. On removal of the benzene the residue was distilled under nitrogen to give a clear oil (35%), b.p. 90-92° at 0.2 mm. Hg. (lit[27], 112° at 0.5 mm. Hg.) shown by ^{31}P N.M.R. to be mainly the required product.

I.r. $\nu_{max_{(cm^{-1})}}$: 1435, 1415 1010 (P-Ph), 960 (P-O-C, ring)

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ : 7.9-7.0 (c, 5H, aromatic protons), 4.3-3.3 (c, 2H, protons α to O), 2.3-1.4 (c, 4H, ring protons) $\delta^{31}P$: +110.4 (lit[173], +110.2).

18. 1-Phenyl-3-methylphosphol-3-ene

Isoprene (13g, 0.19 mol), phenylphosphonous dibromide (50g, 0.19 mol) and cupric stearate (0.52g, 4% by wt. of isoprene) were reacted after the method of Quin et al[168]. The solid formed after 15 hr. was broken up and washed, in the dry box, with dry hexane This adduct (67.2g, 0.185 mol) was then allowed to react with magnesium (4.5g, 0.185 mol) in dry tetrahydrofuran, in a 250 ml round-bottomed flask fitted with condenser and nitrogen line. Heat was applied to commence reaction which then continued without further heating. The reaction mixture was then heated at reflux for 24 hours once this reaction had subsided.

On cooling, the reaction mixture was treated carefully with an excess of saturated sodium bicarbonate solution and then continuously extracted with benzene for a further 24 hours. The benzene solution was then dried, the benzene removed and the residue distilled to give a clear mobile oil (40.3%), b.p. 80° at 0.45 mm. Hg. (lit[168], 125° at 14 mm).

I.r. $\nu_{max_{(cm^{-1})}}$: 1650 (H-C=C), 1430 and 1020 (P-Ph)

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ : 7.1-7.7 (c, 5H, aromatic protons), 5.5 (d, 1H, J_{PH} = 8.0 Hz), 2.0-3.15 (c, 4H, ring protons), 1.80 (s, 3H, methylprotons).

$\delta^{31}P$: -16.69.

19. 1-Phenyl-3-methylphosphol-2-ene

1-Phenyl-3-methylphosphol-2-ene was prepared from isoprene, phenylphosphonous dichloride and cupric stearate as in 18 above. After reaction with magnesium the cooled reaction mixture was treated carefully with cold water once half the tetrahydrofuran had been removed. The solution was then made basic with 10N sodium hydroxide solution and extracted several times with benzene. The benzene extracts were dried, the benzene removed and the residue distilled under nitrogen to give a clear mobile oil (13%), b.p. 84-6° at 0.6 mm. Hg. (lit[168], 79-80 at 0.05 mm).

I.r. $\nu_{max_{(cm^{-1})}}$: 1610 (C=C), 1430 and 1025 (P-Ph)

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ : 7.7-7.0 (c, 5H, aromatic protons), 6.1-5.4 (d, 1H, J_{PH} = 40 Hz), 2.8-1.7 (c, 4H, ring protons), 2.0 (s, 3H, methyl protons).

$\delta^{31}P$: +3.95.

20. 2-Phenyl-1,3,2-benzodioxaphosphole

2-Phenyl-1,3,2-benzodioxaphosphole was prepared by the method of Berlin and Nagabhushanam[154] using the literature quantities of catechol and dichlorophenylphosphine. Removal of solvent yielded white needles (32%), m.p. 140-147° (lit[154], 140-145°), which were washed with benzene.

I.r. $\nu_{max_{(cm^{-1})}}$: 1595 and 1605 (aromatic C=C0, 1440 and 1010 (P-Ph), 1240-1200 ((P)-0-C), 865 and 850 (P-0-(C)).

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ : 8.1-7.2 (c, 5H, phenyl aromatic protons), 7.2-6.7 (c, 4H, aryl aromatic protons).

M.s. Found: parent ion m/e; 324

Calculated for $C_{12}H_9O_2P$: m/e; 216.

Appearance of parent ion at 324 mass units suggests dimerisation in the spectrometer, as the m.p. is as given in the literature.

21. 1-Phenyl-2,2,3-trimethylphosphetan

3,3-Dimethyl-1-butene (20g, 0.24 mol), aluminium trichloride (0.24 mol) and dichlorophenylphosphine (0.24 mol) were allowed to react in methylene chloride by the method of Cremer and Chorvat[174].

— This reaction yielded 1-phenyl-2,2,3-trimethylphosphetan 1-oxide as a white crystalline solid (20%), m.p. 82-3° (lit[174], 81-3°)

I.r. $\nu_{max_{(cm^{-1})}}$: 1440 and 1030 (P-Ph), 1205 (P=0)

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ : (major isomer) 8.1-7.3 (c, 5H, aromatic protons), 3.2-1.9 (c, 3H, ring protons), 1.5 and 1.25 (d, 3H, methyl trans to P=0 in α posn, J_{PH} = 20 Hz), 1.2 and 1.1 (d, 3H, β methyl, J_{PH} = 6 Hz).

M.s. Found: parent ion m/e; 208

Calculated for $C_{12}H_{17}OP$: m/e; 208

Analysis Found: C, 69.3; H, 8.3%

Calculated for $C_{12}H_{17}OP$: C, 69.2; H, 8.2%

The oxide (5g, 0.024 mol) was then deoxygenated with trichlorosilane following the same literature method as above. Distillation gave a clear oil (52%), b.p. 68-71° at 2 mm (lit[174], 71° at 0.3 mm).

I.r. $\nu_{max_{(cm^{-1})}}$: 1435 and 1030 (P-Ph)

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ : 7.9-6.8 (c, 5H, aromatic ring protons), 3.1-1.6 (c, 3H, phosphetan ring protons), 1.5 and 1.2 (d, 3H, methyl trans to P-lone pair, J_{PH} = 20 Hz), 0.9 and 0.8 (d, 3H, other α methyl group, J_{PH} = 8 Hz), 0.8 and 0.7 (d, 3H, β-methyl group, J_{PH} = 6 Hz).

22. 1,3-Diphenylphosphetan

1,3-Diphenylphosphetan was prepared from α-methylstyrene, aluminium trichloride and dichlorophenylphosphine as in 21 above. The oxide was isolated as a viscous opaque oil showing the following characteristics.

I.r. $\nu_{max_{(cm^{-1})}}$: 1435 and 1030 (P-Ph), 1600-1580 (aromatic C=C).

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ: 7.7-6.4 (c, 10H, aromatic ring protons), 2.9-0.6 (c, 5H, small ring protons).

Deoxygenation of the oil with trichlorosilane as in 21 gave a clear oil (12.6%), showing the following characteristics.

I.r. $\nu_{max(cm^{-1})}$: 1435 and 1030 (P-Ph), 1600-1580 (aromatic C=C).

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ : 7.4-6.8 (c, 10H, aromatic ring protons), 2.9-0.3 (c, 5H, phosphetan ring protons)

Further characterisation was not attempted but the iminophosphetan prepared in an attempt to obtain a solid for more careful analysis.

23. 2,2-Dimethylphosphetan

As in 22 above, 2-methyl-1-butene (11.75g, 0.17 mol) dichlorophenylphosphine (25g, 0.14 mol) and aluminium trichloride (18.6g, 0.14 mol) were allowed to react in methylene chloride as solvent. After reaction the crude product (5g, 0.026 mol) was deoxygenated with trichlorosilene (3.52g, 0.026 mol) in the presence of triethylamine in benzene as solvent. Following reaction, the mixture was washed 4 times with saturated sodium chloride solution and dried over magnesium sulphate. The mixture was then filtered and solvent removed giving an opaque oil (0.25g, 5.4%).

As yield was so low, the product was not distilled but taken directly to reaction with azide in an attempt to obtain crystals for characterisation.

The crude product showed the following characteristics however,

I.r. $\nu_{max(cm^{-1})}$: 1440 (P-Ph), 930 (P-ring)

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ : 8.6-7.1 (c, 5H, aromatic protons), 2.3-1.5 (c, ring protons)
(Some impurity present).

24. 2,3-Dimethylphosphetan

As in 22, 3-methyl-1-butene (16.66g, 0.24 mol), dichlorophenylphosphine (42.54g, 0.24 mol) and aluminium trichloride (31.61g, 0.24 mol) were allowed to react in methylene chloride. Following reaction the material was directly allowed to react with trichlorosilene (32.24g, 0.24 mol) in the presence of triethylamine (24.04g, 0.24 mol) in benzene as solvent. The reaction mixture was then worked up as before and once again as in 23 a small yield (4.6%) was achieved of a crude material which was reacted immediately with azide to give the iminophosphetan in an attempt to characterise it.

25. 1,2,3-Triphenyl-1,3,2-diazaphospholidene

N,N'-Diphenylethylenediamine (0.02 mol) was dissolved in xylene (50 ml) and triethylamine (0.04 mol) and allowed to react with dichlorophenylphosphine after the method of Zückerman and Das[175]. On removal of xylene after filtration, the solid residue was recrystallised from benzene, washed with benzene/petrol-ether (40-60) and dried to give white crystals of 1,2,3-triphenyl-1,3,2-diazaphospholidene (39%), m.p. 235-237° (lit[175], 236-238°).

N.m.r. (^{1}H, 60 MHz, $CDCl_3$)δ : 8.0-6.7 (c, aromatic protons), 4.0, 3.9, and 3.5 (ring protons).

26. 2-Methoxy-3-methyl-1,3,2-oxazaphospholan

2-Methylamino-ethanol (20g, 0.27 mol) was allowed to react in benzene with phosphorus trichloride (36.6g, 0.27 mol) in the presence of triethylamine (0.54 mol) with cooling. The residual reaction mixture was then treated with methanol (8.5 g) dropwise with stirring. The triethylamine hydrochloride formed was filtered off, the benzene removed and the residue distilled to give a clear oil (45%) b.p. 55° at 0.4 mm

I.r. ν_{max} $_{(cm^{-1})}$: 2820-2780 (N-Me), 1020 (P-O-Alkyl), 930 (ring).

N.m.r. (^{1}H, 60 MHz, $CDCl_3$) δ : 4.7-4.0 (c, 2H, ring protons), 3.9-3.5 (c, 1H, ring proton), 3.5 and 3.3 (d, 3H, methoxyl protons, J POCH = 10 Hz), 3.2-2.9 (c, 1H, ring proton), 2.85 and 2.6 (d, 3H, methyl protons, JPNCH = 16 Hz).

27. 2-Phenyl-3-Methyl-1,3,2-oxazaphospholan

2-Phenyl-3-Methyl-1,3,2-oxazaphospholan was prepared by the reaction of 2-methylamino-ethanol (20g, 0.27 mol), with dichlorophenylphosphine (47.7g, 0.27 mol) in the presence of triethylamine as in the method of Hudson et al[177]. Distillation gave the product (34%) as a yellowish oil, b.p. 88° at 0.3 mm Hg.

N.m.r. (^{1}H, 60 MHz, $CDCl_3$) δ : 8.0-6.8 (c, 5H, aromatic ring protons), 3.6-2.7 and 2.7-2.0 (c, 7H, ring and N-Me protons, JPNCH = 8Hz).

28. Diethyl phenylphosphonite

The method used was that of Green and Hudson[178], by the reaction of sodium ethoxide (from Na (23g) in EtOH,RR (250 ml)) and dichlorophenylphosphine (44.7 g; 34 ml), added dropwise with cooling. The mixture was stirred overnight at room temperature, when the sodium chloride was filtered off, the filtrate concentrated and distilled to give a clear oil (40%), b.p. 76-80° at 2.5 mm Hg. (lit[178], 76-8° at 0.5 mm).

I.r. $\nu_{max_{(cm^{-1})}}$: 1435 (P-Ph), 1050-1030 (P-O-alkyl).

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ : 7.8-7.3 (c, 5H, ring protons), 4.2-3.6 (c, 4H, $-OCH_2$), 1.5-1.3 (t, 6H, $-CH_3$).

M.s. Found: parent ion m/e; 198

Calculated for $C_{10}H_{15}O_2P$: m/e; 198.

29. Ethyl(2'-bromomethylbenzyl)phenylphosphinate

Diethyl phenylphosphonite (0.06 mol) was added to α,α'-dibromo-o-xylene (0.06 mol) at 90° with stirring as ethyl bromide was distilled from the reaction mixture as in the method of Chan and Nwe[179]. The reaction mixture was then heated for a further 2 hours at this temperature and then chromatographed on a silica gel column using ethyl acetate as eluent. The product (28%) was obtained as white crystals which were dissolved in chloroform to which n-hexane was added till a precipitate just re-appeared. After cooling the crystals, m.p. 97-99° (lit[179], 93-95°) were filtered off and dried.

I.r. $\nu_{max_{(cm^{-1})}}$ KBr : 1590 (aromatic C=C), 1440 (P-Ph), 1205 (P=O), 1025 (P-O-alkyl).

N.m.r. (^{1}H, 60 MHz, $CDCl_3$) δ : 7.9-7.4 (c, 5H, ring protons P-Ph), 7.4-6.8 (c, 4H, ring protons), 4.6 (s, 2H, CH_2Br protons), 4.3-3.8 (q, 2H, $-OCH_2$, J_{POCH} = 2 Hz), 3.7 and 3.4 (d, 2H, P-CH_2 protons, J_{PCH} = 17 Hz), 1.5-1.2 (t, 3H, $-OCH_3$ protons).

M.s. Found: parent ion m/e; 354(^{81}Br) and 352(^{79}Br

Calculated for $C_{16}H_{18}O_2PBr$: m/e; 354(^{81}Br) and 352(^{79}Br

30. 2-Phenyl-iso-phosphindolene

To a stirred solution of ethylene(2'-bromomethylbenzyl) phenylphosphinate (5g) in dry benzene (70 ml) at room temperature, under nitrogen was added dropwise, trichlorosilane (5.9g) in dry benzene (30 ml) after Chan and Nwe[179]. The reaction mixture was then heated at reflux for 48 hours, cooled and hydrolysed with 30% sodium hydroxide solution, the hydroxide being added till no further efforvescence was observed. The silicate formed during the reaction was filtered off and and filtrate washed twice with water. The organic layer was then dried over $MgSO_4$ and passed down a dry 10% deactivated silica column using diethyl ether as eluent. The product in the lower part of the column was collected but proved to be of too low a yield for characterisation as 2-Phenyl-iso-phosphindolene-2-oxide.

Further reaction of this product with trichlorosilane to give the parent phosphine was not, therefore, attempted.

31. Methylphosphonous Dichloridite

Methanol (4.7g, 0.146 mol) was added dropwise with vigorous stirring to phosphorus trichloride (20g, 0.146 mol) at 0° and left stirring overnight at room temperature[180,181]. The reaction mixture was then distilled twice past glass helices to give a clear mobile oil (48-55%), b.p. 92-3° at 760 mm (lit[180,181], 92-3° at 760 mm).

I.r. $\nu_{max(cm^{-1})}$: 1220 and 1210 (P-O-alkyl).

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ : 4.0 and 3.8 (d, 3H, methoxyl protons, J_{PH} = 10 Hz).

32. 1,2,5-Triphenylphosphol-2-ene

An attempt was made to prepare the named material from 1,4-diphenylbuta-1,3-diene and dichlorophenylphosphine in THF in the presence of magnesium after the method of Quin and Mathewes[185] with slight variation.

A slurry of the diene (14.4g, 0.07 mol) in THF was placed in a 500 ml round bottomed flask, flushed with nitrogen and magnesium added. The flask was fitted with condenser, nitrogen line and dropping funnel as well as magnetic stirrer. The dichlorophenylphosphine (12.5g, 0.07 mol) was then added dropwise with stirring while the flask was heated slightly to initiate reaction. After apparent reaction had subsided the reaction mixture was refluxed for 2 hours. On cooling white hexagonal crystals formed of unreacted diene. The residual mixture was then washed up with cold water and sodium hydroxide. No material characterisable as the named product was obtainable.

33. 1-Phenylphosphiran

Attempts to prepare the named material by the method of Chan et al[186] did not lead to characterisable quantities of any product.

34. 2-Methyl-1,3,2-dioxaphospholan

Attempts to prepare this material from 2-methoxy-1,3,2-dioxaphospholan via an Arbusov Reaction with methyl iodide followed by de-oxygenation of the oxide with trichlorosilane met with no success.

35. 1-Phenyl-3,3-dimethylphosphol-2-ene

The preparation of this material was attempted using the method of Trippett et al[184] by allowing 1-phenyl-2,2,3-trimethylphosphetan oxide (19.1g, 0.093 mol) to react with trichlorosilane (12.6g, 0.093 mol) and triethylamine (9.4g, 0.093 mol) in methylene chloride as in B21.

Work-up of the reaction mixture as in B21 yielded the trivalent 1-phenyl-2,2,3-trimethylphosphetan (4.26g) which was then treated in methylene chloride at -20° with 1 equivalent of bromine, left standing overnight under nitrogen and then distilled to give 1g (16%) of a yellow liquid, b.p. $142\text{-}4^{\circ}$ at 10 mm Hg which is the ring opened bromide giving the following characteristics:

I.r. $\nu_{max_{(cm^{-1})}}$: 1440 and 1020 cm^{-1} (P-Ph), 690 (P-Br), 1590 (C=C).

N.m.r. (^{1}H, 60 MHz, $CDCl_3$) δ : 8.1-7.2 (c, 6H, aromatic and olefinic protons), 3.3-2.9 (c, 1H, other olefinic proton), 2.2-0.7 (c, 9H, methyl and aliphatic protons).

M.s. Found: parent ion m/e; 292(^{81}Br) and 270(^{79}Br)
Calculated for $C_{12}H_{16}PBr$ parent ion m/e;
292(^{81}Br) and 270(^{79}Br)

This material was then treated with 1 equivalent of alkali, this being sodium ethoxide in ethanol (0.1g Na in 10 ml super-dry ethanol added to 0.95 g of compound in dry benzene). Solvent was then removed and the reaction mixture distilled to give 0.85g (4.8%) of a colourless liquid b.p. 82-84^o at 0.2 mm Hg.

36. 1-Phenyl-phosphol-2-ene

An adduct of dichlorophenylphosphine and buta-1,3-diene was prepared after the method of Quin et al[176,177] and made up in THF. This adduct solution was then added portionwise with vigorous stirring to magnesium turnings in THF. (Reaction is exothermic so some control with an ice bath may be necessary.)

The reaction mixture was then heated under reflux for 1 hour at least after the end of the reaction, treated slowly with water (cold) to destroy any remaining phosphorus chlorides and made strongly acidic with 8N HCl to destroy any remaining magnesium. THF was removed by distillation, the reaction mixture made basic with concentrated sodium hydroxide and steam distilled.

The product was extracted from the distillate with ether, dried with sodium sulphate and distilled at atmospheric pressure.

A clear oil was collected at 130°, 0.2g (16.4%).

N.m.r. (^{1}H, 60 MHz, $CDCl_3$) δ: 7.2-6.8 (m, 6H, aromatic ring protons and α PCH ring proton (?)), 2.4-2.2 (5H, ring protons and β -PCH proton (?)).

C. Preparation of o-Nitroaryl-iminophosphines

1. N-(4-methoxy-2-nitrophenyl)-imino-1,2,5-triphenylphosphole

1,2,5-Triphenylphosphole (2.02g, 0.007 mol) was placed in dry toluene (75 ml) with 4-azido-3-nitroanisole (1.51g, 0.008 mol). The reaction mixture was then heated to 100°, under nitrogen, until gas evolution ceased. The solvent was then removed in vacuo and the product recrystallised from chloroform/ether to give blue/black cubes of N-(4-methoxy-2-nitrophenyl)-imino-1,2,5-triphenylphosphole (72%), m.p. 172-173° (lit[9], 172-173°).

I.r. $\nu_{max_{(cm^{-1})}}$: 1510 ($-NO_2$), 1435 and 990 (P-Ph), 1275-1250 (P=N), 1040 (C-O).

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ : 8.4-6.7 (c, 20H, aromatic and phosphole ring protons, 3.65 (s, 3H, methoxyl protons).

M.s. Found parent ion : m/e; 478

Calculated for $C_{29}H_{23}N_2O_3P$: m/e; 478

Analysis Found : C, 73.0%; H, 4.9%; N, 5.7%

Calculated for $C_{29}H_{23}N_2O_3P$:

C, 73.0%; H, 4.85%; N, 5.9%

$\delta^{31}P$: +13.1

2. N-(4-methyl-2-nitrophenyl)-imino-1,2,5-triphenylphosphole

4-Azido-3-nitrotoluene (1.43g, 0.008 mol) was reacted with 1,2,5-triphenylphosphole (2.02g, 0.007 mol) as in 1 above. Removal of solvent and fractional recrystallisation from chloroform/ether gave 1,2,5-triphenylphosphole oxide (1.06g, 46%) and large red cubes of the iminophosphole (1.42g, 44%),

m.p. 154-156° (lit[9], 154-156°).

I.r. $\nu_{max(cm^{-1})}$: 1615 (aromatic C=C), 1490 (NO_2), 1440 and 1000 (P-Ph), 1360-1330 (P=N).

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ: 8.3-6.4 (c, 20H, aromatic and phosphole ring protons), 2.1 (s, 3H, methyl protons).

M.s. Found parent ion : m/e; 462

Calculated for $C_{29}H_{23}N_2O_2P$: m/e; 462

Analysis Found : C, 75.0%; H, 5.1%; N, 5.8%

Calculated for $C_{29}H_{23}N_2O_2P$:

C, 75.4%; H, 5.0%; N, 6.0%

$\delta^{31}P$: +14.28

3. N-(4-methoxy-2-nitrophenyl)-triphenylphosphinimine

Triphenylphosphine (2.0g, 0.008 mol) was allowed to react, on warming, under dry ether, with 4-azido-3-nitroanisole (1.48g, 0.008 mol). On scratching an immediate solid precipitate of pale yellow crystals (62%) of the phosphinimine was formed, m.p. 160-162° (lit[9], 160-162°).

I.r. $\nu_{max(cm^{-1})}$: 1510 (NO_2), 1440 and 1000 (P-Ph), 1280 (P=N), 1110 (C-O).

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ: 8.1-7.4 (c, 15H, P-Ph, aromatic ring protons), 7.3 and 6.6 (c, 3H, N-Ph protons), 3.7 (s, 3H, methoxyl protons).

Analysis Found : C, 69.9%; H, 4.9%; N, 6.7%

Calculated for $C_{25}H_{21}N_2O_3P$:

C, 70.1%; H, 4.9%; N, 6.5%

4. N-(4-methyl-2-nitrophenyl)-imino-2-phenyl-1,3,2-dioxaphospholan

2-Phenyl-1,3,2-dioxaphospholan (3.7g, 0.02 mol) was placed under dry ether under nitrogen and 4-azido-3-nitro toluene (3.5g, 0.02 mol) added portionwise with stirring. Gas evolution was immediately apparent and a yellow oil formed under the ether. On scratching yellow crystals of the imino-phospholan (73%) were formed, m.p. 172-174°, which were dried in a dessicator.

I.r. $\nu_{max_{(cm^{-1})}}$: 1520 ($-NO_2$), 1440 (P-Ph), 1255-1210 (P=N), 910 (ring)

N.m.r. (^1H, 100 MHz, $CDCl_3$) δ: 8.0-6.6 (c, 8H, aromatic ring protons), 4.7-4.1 (d of d, 4H, phospholan ring protons, J_{POCH} = 40 Hz), 2.2 (s, 3H, methyl protons).

M.s. Found parent ion : m/e; 318

$C_{15}H_{15}N_2O_4P$ requires : m/e; 318

Analysis Found : C, 56.9%; H, 4.2%; N, 8.6%

$C_{15}H_{15}N_2O_4P$ requires : C, 56.6%; H, 4.7%, N, 8.8%

$\delta^{31}P$: +23.46

5. N-(4-methoxy-2-nitrophenyl)-imino-2-phenyl-1,3,2-dioxaphospholan

4-azido-3-nitroanisole (2.35g, 0.012 mol) was allowed to react with 2-phenyl-1,3,2-dioxaphospholan (2.0g, 0.012 mol) as in 4 above. Again a yellow solid was obtained on scratching, the yellow crystals (75%), m.p. 184-186° being washed with ether and dried in a dessicator.

I.r. $\nu_{max_{(cm^{-1})}}$: 1515 (NO_2), 1440 (P-Ph), 1260 (P=N), 915 (ring).

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ : 8.0-6.6 (c, 8H, aromatic ring protons), 4.7-4.2 (d of d, 4H, phospholan ring protons, J_{POCH} = 40 Hz) 3.9 (s, 3H, methoxyl protons).

M.s. Found parent ion: m/e; 334

$C_{15}H_{15}N_2O_5P$ requires: m/e; 334

Analysis Found : C, 53.7%; H, 4.4%; N, 8.2%

$C_{15}H_{15}N_2O_5P$ requires : C, 53.9%; H, 4.5%; N, 8.4%

$\delta^{31}P$: +21.1

Note: The following iminophosphorus compounds were not obtained completely pure as they could not be crystallised under any conditions of temperature and solvent attempted and most contained the aniline from the azide considered.

6. N-(4-methyl-2-nitrophenyl)-imino-1-phenylphospholan

1-Phenylphospholan (1.0g, 0.006 mol) was allowed to react with 4-azido-3-nitrotoluene (1.1g, 0.006 mol) as in 4 above, the flask being cooled in a cardice/acetone bath. The reaction mixture was then allowed to come slowly to room temperature. On removal of ether a dark red oil was obtained. The oil would not solidify and attempted distillation gave 5-methylbenzofurazan, as a solid which came out on the sides of the condenser, indicating decomposition. This decomposition was noted even under vacuum distillation conditions in a Kugelrohr. The following details were obtained from the crude oil.

I.r. $\nu_{max(cm^{-1})}$: 1515 (NO_2), 1440 (P-Ph), 1275-1250 (P=N), 855 (phospholan ring).

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ : 7.9-7.3 (c, 5H, P-Ph ring protons), 7.0-6.3 (c, 3H, aromatic ring protons), 2.2-1.3 (c, 8H, ring protons), 1.8 (s, 3H, methyl protons).

M.s. Found parent ion : m/e; 314

$C_{17}H_{19}N_2O_2P$ requires : m/e; 314

Exact mass spectroscopy : $C_{17}H_{19}N_2O_2P$ requires 314. 118408
Found 314. 118260
Error less than 1 ppm.

7. N-(4-methoxy-2-nitrophenyl)-imino-1-phenylphospholan

4-Azido-3-nitroanisole (1.1g, 0.006 mol) and 1-phenyl-phospholan (1.0g, 0.006 mol) were allowed to react under dry ether as in 6 above. The resultant red oil behaved in a similar fashion. The crude oil showed the following characteristics.

I.r. $\nu_{max(cm^{-1})}$: 1510 (NO_2), 1440 and 1040 (P-Ph), 1275 (P=N), 1115 (C-O), 855 (phospholan ring).

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ: 8.0-7.5 (c, 5H, P-Ph ring protons), 7.1-6.7 (c, 3H, aromatic ring protons), 3.8 (s, 3H, methoxyl protons), 2.5-1.8 (c, 8H, phospholan ring protons).

On scratching for a good while a very few leaf-like crystals did appear. Attempted analysis gave the following as a result.

Analysis Found : C, 59.7%; H, 5.9%; N, 8.5%

$C_{17}H_{19}N_2O_3P$ requires : C, 61.8%; H, 5.8%; N, 8.5%

Attempted recrystallisations from ether with scratching gave no improvement.

8. N-(4-methyl-2-nitrophenyl)-imino-2-(N-dimethylamino)-1,3,2-dioxaphosphorinan

N-dimethyl-1,3,2-dioxaphosphorinan (4.9g, 0.033 mol) was placed in toluene under nitrogen and 4-azido-3-nitrotoluene (5.9g, 0.033 mol) was added slowly with stirring. Gas evolution was apparent. On removal of toluene on the high vacuum rotary evaporator an orange oil was obtained which was shown to be the iminophosphorinan by exact mass spectroscopy.

M.s. Found parent ion : m/e; 299

$C_{12}H_{18}N_3O_4P$ requires : m/e; 299

Exact Mass : Found parent ion : m/e; 299. 103203

$C_{12}H_{18}N_3O_4P$ requires : m/e; 299. 103486

Error less than 1 ppm.

The oil also showed the following characteristics.

I.r. $\nu_{max_{(cm^{-1})}}$: 1520 (NO_2), 1280-1240 (P=N), 1000 (P-O-alkyl), 930 (phosphorinan ring), 705 ($P-Nme_2$).

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ : 7.4-6.7 (c, 3H, aromatic ring protons), 4.6-4.0 (c, 4H, phosphorinan ring protons σ to O), 2.8 and 2.6 (d, 6H, Nme_2 protons, J_{PNCH} = 11 Hz), 2.8-1.5 (c, 2H, ring protons), 2.2 (s, 3H, methyl protons).

9. N-(4-methyl-2-nitrophenyl)-imino-2-phenyl-1,3,2-dioxaphosphorinan

4-Azido-3-nitrotoluene was allowed to react in equimolar quantity, with 2-phenyl-1,3,2-dioxaphosphorinan under ether under nitrogen. Gas evolution was immediately apparent. On removal of ether an orange oil was obtained which was shown by exact mass spectroscopy to contain the required iminophosphorinan.

M.s. Found parent ion : m/e; 332

$C_{16}H_{17}N_2O_4P$ requires : m/e; 332

Exact Mass : Found parent ion : m/e; 332. 093164

$C_{16}H_{17}N_2O_4P$ requires : m/e; 332. 092587

Error less than 2 ppm.

The oil also showed the following characteristics.

I.r. $\nu_{max_{(cm^{-1})}}$: 1280-1250 (P=N)

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ: 8.0-7.0 (c, 5H, P-Ph ring protons), 4.7-3.7 (c, 4H, phosphorinan ring protons σ to O), 2.2 (s, 3H, methyl protons), 2.2-1.7 (c, 2H, ring protons).

10. N-(4-methyl-2-nitrophenyl)-imino-1,3-diphenylphosphetan

1,3-Diphenylphosphetan was allowed to react with 4-azido-3-nitrotoluene, in equimolar quantity, under dry ether under nitrogen. Gas evolution was apparent after a few moments. After the reaction had subsided a red oil was obtained which showed the following characteristics.

I.r. $\nu_{max_{(cm^{-1})}}$: 1560 and 1520 (NO_2), 125001210 (P=N).

N.m.r. (^{1}H, 60 MHz, $CDCl_3$) δ: 7.9-6.5 (c, 13H, aromatic ring protons), 3.2-0.8 (c, 5H, phosphetan ring protons), 2.35 (s, 3H, methyl protons).

M.s. No parent ion observed at 376.

$C_{22}H_{21}N_2O_2P$ requires: parent ion m/e; 376.

A peak was observed however at 152 corresponding to 4-methyl-2-nitroaniline and another at 198 which is neither the oxide (m/e 242) or the phosphetan itself (m/e 226) but may be due to decomposition of the phosphetan ring in the spectrometer *via* a migration of the phenyl group and loss of ethylene to give $Ph\overset{+}{C}HPPh$ (m/e 198)

Analysis: This was not attempted as material contained an amine (probably 4-methyl-2-nitroaniline) which could not be separated by crystallisation, distillation or chromatography.

11. N-(4-methoxy-2-nitrophenyl)-imino-1-phenyl-2,2,3-trimethylphosphetan

1-Phenyl-2,2,3-trimethylphosphetan (1.2g, 0.006 mol) was allowed to react with 4-azido-3-nitroanisole (1.1g, 0.006 mol) as in 10 above. Gas evolution was immediate and after the reaction had subsided the ether was removed to yield a red oil showing the following characteristics.

I.r. $\nu_{max_{(cm^{-1})}}$: 1520 (NO_2), 1250-1200 (P=N).

N.m.r. (^{1}H, 60 Mhz, $CDCl_3$) δ: 8.0-6.8 (c, 8H, aromatic ring protons), 3.6 (s, 3H, methoxyl protons), 3.3-2.0 (c, 3H, phosphetan ring protons), 1.6-0.8 (c, 9H, methyl protons).

M.s. Found parent ion : m/e; 360

$C_{19}H_{23}N_2O_3P$ requires : m/e; 358

Exact Mass: The peak at m/e 360 was found to give an exact mass of 360. 163847.

The breakdown pattern gave no major peak at m/e 168 which would be indicative of 4-amino-3-nitroanisole. However, a major peak was observed at m/e 150 corresponding to 5-methoxybenzofurazan, a decomposition product of the iminophosphetan. A further major peak was also observed at 178 which may be a decomposition product of the phosphetan ring.

Attempts at purification of the oil by distillation under nitrogen also gave 5-methoxybenzofurazan as a product.

Note: All the following attempted preparations of iminophosphines gave mass spectra indicating fracture of the phosphorus-nitrogen link to give the phosphine oxide and the corresponding amine. All gave the expected benzofurazan on distillation except 12, 19-21, and 25-27.

12. N-(4-methyl-2-nitrophenyl)-imino-diethylphenylphosphine

Diethylphenylphosphine was allowed to react under dry ether under nitrogen with an equimolar quantity of 4-azido-3-nitrotoluene. Gas evolution was immediate and removal of solvent gave a dark red oil showing the following characteristics

I.r. $\nu_{max(cm^{-1})}$: 1250 (P=N), 1560, 1520 (NO_2).

N.m.r. (^{1}H, 60 MHz, $CDCl_3$) δ: 7.8-7.3 (c, 5H, P-Ph ring protons), 7.3-6.3 (c, 3H, aromatic ring protons), 2.4-2.2 (d, 4H, protons α to P), 1.400.8 (c, 9H, protons β to P and methyl protons).

M.s. $C_{17}H_{21}N_2O_2P$ requires parent ion m/e; 316

Two major peaks were observed at m/e 182 corresponding to diethylphenylphosphine oxide and m/e 152 corresponding to 4-amino-3-nitrotoluene. Parent ion at m/e 316 was not observed.

Analysis: Impurities in the oil precluded any attempt at analysis. Attempted purification by distillation gave a black tar.

13. <u>N-(4-methoxy-2-nitrophenyl)-imino-1-phenyl-3-methylphosphol-2-ene</u>

1-Phenyl-3-methylphosphol-2-ene (1.09g, 0.006 mol) was allowed to react with 4-azido-3-nitroanisole (1.2 g, 0.006 mol) as in 12. Gas evolution was immediately apparent. Removal of solvent yielded a red oil showing the following characteristics.

I.r. $\nu_{max(cm^{-1})}$: 1610 (C=CH), 1440 (P-Ph), 1250-1170 (P=N), 1120 (C-O).

N.m.r. (^{1}H, 60 MHz, $CDCl_3$) δ: 9.9-6.6 (c, 8H, aromatic ring protons), 5.8 and 5.2 (d, 1H, C=CH, J_{PCCH} = 32 Hz), 3.8 (s, 3H, methoxyl protons), 2.9-2.3 (c, 4H, ring protons), 1.8 (s, 3H, methyl protons).

M.s. $C_{18}H_{19}N_2O_3P$ requires parent ion m/e; 342

Parent ion not observed. Major peaks were observed however at m/e 192 corresponding to the phosphine oxide and m/e 168 corresponding to 4-amino-3-nitroanisole.

Analysis: This was precluded by evidence of amine impurity evident in the i.r. spectrum. Distillation gave 5-methoxybenzofurazan.

14. N-(4-methoxy-2-nitrophenyl)-imino-1-phenyl-3-methylphosphol-3-ene

Reaction of 1-phenyl-3-methylphosphol-3-ene and 4-azido-3-nitroanisole in equimolar quantities as in 13 yielded a red oil showing similar characteristics.

I.r. $\nu_{max_{(cm^{-1})}}$: 1610 (C=CH), 1510 (NO_2), 125001170 (P=N), 1120 (C-O).

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ: 7.9-6.7 (c, H, aromatic ring protons), 6.15 and 5.7 (d, C=CH, J_{PCCH} = 25 Hz), 3.9 (s, 3H, methoxyl protons), 3.0-2.0 (c, 4H, ring protons), 2.1 (s, 3H, methyl protons).

M.s. $C_{18}H_{19}N_2O_3P$ requires: parent ion m/e; 342
Parent ion not observed. Major peaks were observed at m/e 192 corresponding to the phosphine oxide and m/e 168 corresponding to the 4-amino-3-nitrotoluene.

Analysis: Again amine presence was indicated by i.r. spectroscopy. Distillation again gave 5-methoxybenzofurazan as a product.

15. N-(4-methoxy-2-nitrophenyl)-imino-(2-N-dimethyl)-1,3,2-dioxaphospholan

2-N-dimethyl-1,3,2-dioxaphospholan and 4-azido-3-nitroanisole were reacted as in 13. The resultant red oil gave similar behaviour on distillation, and the following characteristics were noted.

I.r. $\nu_{max_{(cm^{-1})}}$: 1270-1200 (P=N).

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ: 7.7-6.9 (c, 3H, aromatic ring protons), 4.6-3.6 (c, 4H, phospholan ring protons), 3.8 (s, 3H, methoxyl protons), 2.9 (d, 6H, $-NMe_2$ protons, J_{PNCH} = 11Hz).

M.s. $C_{11}H_{16}N_3O_5P$ requires parent ion m/e; 301

Parent ion was not observed, however, peaks were observed for m/e 168 corresponding to 4-amino-3-nitroanisole, m/e 150 corresponding to 5-methoxybenzofurazan, m/e 151 corresponding to 2-N-dimethyl-1,3,2-dioxaphospholan oxide and m/e 135 corresponding to 2-N-dimethyl-1,3,2-dioxaphospholan itself suggesting decomposition in the spectrometer.

16. N-(4-methoxy-2-nitrophenyl)-imino-1,2,3-triphenyl-1,3,2-diazaphospholidene

4-Azido-3-nitroanisole (0.4g, 0.002 mol) and 1,2,3-triphenyl-1,3,2-diazophospholidene (0.65g, 0.002 mol) were allowed to react under toluene as in 1. Removal of toluene under vacuum gave a pale grey flaky solid (31%). Attempted recrystallisation from chloroform/ether gave a pale white solid showing the following characteristics.

I.r. $\nu_{max(cm^{-1})}$: 1620, 1600, 1590 (Aromatic C=CH), 1540 and 1500 (NO_2), 1270-1200 (P=N), 1120 (C-O).

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ : 8.0-6.8 (c, 18H, aromatic ring protons), 4.0 and 3.85 (d, 4H, phospholidene ring protons), 3.9 (s, 3H, methoxyl protons).

M.s. $C_{27}H_{25}N_4O_3P$ requires parent ion m/e; 484.

This was not observed. However, m/e 334 corresponding to 1,2,3-triphenyl-1,3,2-diazaphospholidene-2-oxide was observed as was m/e 166 corresponding to the nitrene fragment from decomposition of the expected parent by cleavage of the P-N bond, and m/e 150 corresponding to 5-methoxybenzofurazan, one of the decomposition products of the iminophosphines under study.

17. <u>N-(4-methyl-2-nitrophenyl)-imino-1-phenylphosphorinan</u>

1-Phenylphosphorinan (5.0g, 0.028 mol) and 4-azido-3-nitrotoluene (5.0g, 0.028 mol) were allowed to react under dry ether as in 4 above. Gas evolution was immediately apparent and on removal of ether a viscous red oil was obtained which yielded 5-methylbenzofurazan on attempting distillation. The oil gave the following results.

I.r. $\nu_{max(cm^{-1})}$: 1620, 1600 (aromatic ring C=CH), 1520 (NO_2), 1250 (P=N), 920 (phosphorinan ring).

N.m.r. (^{1}H, 60 MHz, $CDCl_3$) δ: 7.8-6.3 (c, 8H, aromatic ring protons), 3.3-2.6 (c, 4H, phosphorinan ring protons α to P), 1.3-0.5 (c, 6H, ring protons β and γ from P), 2.1 (s, 3H, methyl protons).

M.s. $C_{18}H_{21}N_2O_2P$ requires parent ion m/e; 328.

This was not observed. Peaks at m/e 194 corresponding to 1-phenylphosphorinan-1-oxide and m/e 152 corresponding to 4-amino-3-nitrotoluene were observed.

18. <u>N-(4-methyl-3-nitrophenyl)imino-1-methyl-2-methoxy-1,3,2-azoxaphospholan</u>

1-Methyl-2-methoxy-1,3,2-azoxaphospholan and 4-azido-3-nitrotoluene in equimolar amounts were allowed to react under ether as in 4 above. Gas evolution was immediately apparent with removal of solvent yielding an orange oil showing the following characteristics.

I.r. $\nu_{max(cm^{-1})}$: 1540 and 1500 (NO_2), 1280-1210 (P=N), 910 (ring).

N.m.r. (^{1}H, 60 MHz, $CDCl_3$) δ: 8.0-6.8 (c, 3H, aromatic ring protons), 4.5-4.0 (phospholan ring proton), 3.8-3.1 (c, 5H, ring protons and P-methoxyl protons), 3.0-2.4 (c, 4H, ring proton and PN methyl protons), 2.2 (s, 3H, methyl protons).

M.s. $C_{11}H_{15}N_3O_4P$ requires parent ion m/e; 285.

Parent ion not observed. However, m/e 152 corresponding to 4-amino-3-nitrotoluene and m/e 271 (which may correspond to loss of methyl and gain of one proton on the azoxaphospholan ring) were observed. 5-Methylbenzofurazan was obtained on distillation.

19. N-(4-methyl-2-nitrophenyl)-triethylphosphorimidate

Triethylphosphite (freshly distilled, 2.00g, 0.012 mol) was allowed to react in light-petrol (40:60) with 4-azido-3-nitrotoluene (2.14g, 0.012 mol). Gas evolution was immediately apparent. Removal of solvent gave a viscous yellow oil which was rapidly eluted down a short alumina column in a 50/50 ether/light-petrol mixture to give a reddish orange oil (74%).

N.m.r. (^{1}H, 60 MHz, $CDCl_3$) δ : 7.5-6.7 (c, 3H, aromatic ring protons), 4.4-3.9 (d.of q., 6H, $-CH_2-O$ protons, J_{POCH} = 7 Hz), 2.3 (s, 3H, methyl protons), 1.5-1.2 (t, 9H, methyl protons of ethoxy groups).

The i.r. spectrum shows a large absorption in the region of 1250 cm^{-1}. Material is similar in character to the N-(2-nitrophenyl)-triethylphosphorimidate prepared by R.J. Scott.[9]

20. N-(4-methoxy-2-nitrophenyl)-imino-9-phenyl-9-phosphafluorene

9-phenyl-9-phosphafluorene prepared by R.J. Scott[9] was allowed to react in equimolar quantity with 4-azido-3-nitroanisole under dry ether. Gas evolution was soon apparent. A yellow solid (21%) precipitated from solution, showing the following characteristics:

I.R. $\nu_{max_{(cm^{-1})}}$: 1560 and 1510 (NO_2), 1440 and 1000 (P-Ph), 1280-1250 (P=N), 1045 (C-O).

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ: 8.107.2 (c, 13H, aromatic protons, P-Ph and phosphafluorene ring protons), 7.0-6.2 (c, 3H, N-Aryl aromatic ring protons), 3.7 (s, 3H, methoxyl protons).

Analysis was unsatisfactory due to the presence of an impurity, probably 4-amino-3-nitroanisole, which it was found unable to remove even after 3 or 4 recrystallisations from ether.

21. N-(4-methyl-2-nitrophenyl)-imino-9-phenyl-9-phosphafluorene

This material was prepared in the same manner as in 20 by the reaction of 9-phenyl-9-phosphafluorene with 4-azido-3-nitrotoluene in equimolar amounts under ether. Again a

yellow/orange solid was formed (25%) which had similar N.m.r. characteristics, viz:

N.m.r. (^{1}H, 60 MHz, $CDCl_3$) δ: 8.1-7.2 (c, 13H, aromatic ring protons), 6.8-6.0 (c, 3H, aromatic ring protons), 2.2 (s, 3H, methyl protons).

Once more an impurity excluded satisfactory analysis despite several attempts at recrystallisation.

Both the 4-methoxy- and 4-methyl-substituted materials had similar characteristics to the unsubstituted material prepared by R.J. Scott.

22. N-(methyl-2-nitrophenyl)-imino-trichlorophosphorane

4-Methyl-2-nitroaniline hydrochloride (4.52 g, 0.024 mol) and phosphorus pentachloride (8.34 g, 0.04 mol) were placed in dry toluene under nitrogen, under reflux until gas evolution ceased. Dry petrol was then added as in the method of R.J. Scott[9], and precipitated material discarded. The filtered solution was then placed in a tightly-sealed flask and stored at 0°C for several days. No material crystallised as in R.J. Scott's preparation of the unsubstituted N-aryl-trichlorophosphorane.

23. N-(4-methoxy-2-nitrophenyl)-imino-2-acyloxy-1,3,2-dioxaphospholan

2-Acyloxy-1,3,2-dioxaphospholan and 4-azido-3-nitroanisole were allowed to react in equimolar quantities under dry ether as in 6 above. Gas evolution was immediately apparent and a yellow flaky solid precipitated from solution. Before the

ether was removed however this rapidly turned orange and then decomposed to a viscous red/orange oil, shown by N.m.r. to be a mixture of at least two components. On standing in the dry-box overnight red crystals of 4-amino-3-nitroanisole were formed.

24. N-(4-methyl-2-nitrophenyl)-imino-2-phenyl-1,3,2-benzodioxaphosphole

Attempts to prepare this material from 4-azido-3-nitrotoluene and 2-phenyl-1,3,2-benzodioxaphosphole met with no success and no gas evolution or reaction appeared to take place in toluene just below boiling point. When heated in benzene at 80° a red solution was obtained but this was due to decomposition of the azide only to the amine.

25. N-(2-N-oxypyridyl)-imino-1-phenylphospholan

1-Phenylphospholan (0.8 g, 0.005 mol) was added in ether solution to 2-azido-pyridine-1-oxide (0.4 g, 0.005 mol) in ether, when nitrogen evolution was apparent. Removal of the ether gave an oil which solidified on addition of the minimum of ether to give N-(-2-N-oxypyridyl)-imino-1-phenylphospholan (59%) as a brownish crystalline powder, m.p. 145-152°.

I.r. $\nu_{max(cm^{-1})}$: 1605 (aromatic C=C), 1440 (P-Ph), 1365 (P=N), 1185 (n-oxide).

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ: 7.8-6.2 (c, 9H, aromatic protons), 3.0-1.5 (c, 8H, phospholan ring protons).

M.s. Found, parent ion : m/e; 272

$C_{15}H_{17}N_2OP$ requires : m/e; 272.

$\delta\,^{31}P$: 42.18

26. N-(2-N-oxypyridyl)-imino-triphenylphosphine

Triphenylphosphine (1.45 g, 0.006 mol) and 2-azido-pyridine-1-oxide (0.75 g, 0.006 mol) were reacted as in 25 above. Removal of ether and recrystallisation from chloroform/ether gave an off-white crystalline powder (78%) shown to be N-(2-N-oxypyridyl)-imino-triphenylphosphine, m.p. 185-188°.

I.r. $\nu_{max_{(cm^{-1})}}$: 1605 (aromatic C=C), 1435 and 1000 (P-Ph), 1375 (P=N), 1190 (N-oxide).

N.m.r. (^1H, 60 MHz, $CDCl_3$) δ: 8.0-6.2 (c, aromatic ring protons), $\delta\,^{31}P = +13.24$.

M.s. Found, parent ion m/e = 370

$C_{23}H_{19}N_2OP$ requires m/e = 370.

$\delta^{31}P$: +13.24

Analysis: Found C 74.4%, H 5.25%, N 7.6%

$C_{23}H_{19}N_2OP$ requires C 74.6%, H 5.1%, N 7.6%.

27. N-(2-N-oxypyridyl)-imino-1,2,5-triphenylphosphole

1,2,5-Triphenylphosphole (2.29 g, 0.007 mol) was placed under toluene in a nitrogen flushed flask and 2-azido-pyridine-1-oxide (1 g, 0.007 mol) added. The reaction mixture was then heated to 90-100° when gas evolution was apparent. On cooling, the toluene was removed in vacuo and the residue recrystallised from the minimum of toluene. Yellow crystals of 1,2,5-triphenylphosphole (2.25 g) were recovered, showing no reaction. Abramovitch and Cue have shown that the azide thermolyses below 100°, so presumably the phosphole was not reactive enough as a nitrene trap.

28. N-(4-methoxy-2-nitrophenyl)-imino-2-methoxy-1,3,2-dioxaphospholan

2-Methoxy-1,3,2-dioxaphospholan (5.05g, 0.04 mol) was allowed to react under dry ether with 4-azido-3-nitroanisole (7.12g, 0.04 mol) when nitrogen evolution was immediately apparent. On removal of solvent, a red oil was obtained which from i.r. and N.m.r. data obviously contained 4-amino-3-nitroanisole but also gave the following i.r. characteristics, viz:

$\nu_{max(cm^{-1})}$: 1530 and 1490 (NO_2), 1340 (P=N), 920-910 (ring and P-O- alkyl).

29. N-(4-methyl-2-nitrophenyl)-imino-3-methyl-2-phenyl-1,3,2-oxazaphospholan

3-Methyl-2-phenyl-1,3,2-oxazaphospholan (1.8g, .01 mol) was allowed to react under dry ether with 4-azido-3-nitrotoluene (1.75g, 0.01 mol) when nitrogen evolution was apparent. On removal of solvent a viscous red oil was recovered showing the following i.r. characteristics, viz:

$\nu_{max(cm^{-1})}$: 1440 (P-Ph), 1530 and 1500 ($-NO_2$), 1350-1310 (P=N), 900-910 (P-NMe and ring).

30. N-(4-methyl-2-nitrophenyl)-imino-1-phenyl-2,2-dimethylphosphetan

1-Phenyl-2,2-dimethylphosphetan (crude) was allowed to react with 4-azido-3-nitrotoluene as in 11. Removal of solvent gave a deep red oil showing the following characteristics by N.m.r.

N.m.r. (^{1}H, 60 MHz, $CDCl_3$) δ: 7.8-6.8 (m, 8H, aromatic protons), 2.4-0.6 (s and m, 13H, methyl and ring protons).

31. N-(4-methyl-2-nitrophenyl)-imino-1-phenyl-2,3-dimethylphosphetan

1-Phenyl-2,3-dimethylphosphetan (crude) was allowed to react with 4-azido-3-nitrotoluene under dry ether. Nitrogen evolution was immediately apparent. Removal of solvent gave a deep red oil, which was too impure for any attempt at identification.

32. N-(4-methyl-2-nitrophenyl)-1-phenylphosphol-2-ene

1-Phenylphosphol-2-ene (crude) was allowed to react with 4-azido-3-nitrotoluene under dry ether as in 31. Nitrogen evolution was apparent and a very small amount of impure red oil was obtained.

Note: Materials 28-32 were all allowed to undergo decomposition at 160° in a sealed N.m.r. tube. In all cases a peak corresponding to 5-methyl(or methoxy) benzofurazan and the corresponding aniline were observed and kinetic studies gave remarkably good straight line results for first order reactions, which being independent of concentration are not affected by impurity. The results obtained from each solution were consistent with the general pattern otherwise observed.

D. Thermal Decomposition Reactions and Kinetic Studies by N.M.R.

The Imino-phosphorus compounds prepared were heated at 160°C, in bromobenzene solution, in sealed N.m.r. tubes, and the kinetics of decomposition followed by ^{1}H and/or ^{31}P N.m.r. spectroscopy.

^{1}H N.m.r. Kinetics

Approximately 80-100 mg. of iminophosphorus material was used per N.m.r. tube, using the appropriate amount of dry toluene or dry anisole as internal standard. The N.m.r. tubes were loaded in the dry box, after being dried in the vacuum oven, and then de-gassed and sealed on a vacuum line. The N.m.r. spectrum of the material was then taken, at appropriate intervals, at room temperature, as no reaction occurs at this temperature.

^{31}P N.m.r. Kinetics

N.m.r. tubes were made up in the same way as for the ^{1}H N.m.r. kinetics, using t-butylbenzene as solvent, which contained approximately 20 per cent of d_6-benzene as a lock signal. Triethyl phosphate was found to be a useful internal standard.

Whereas for the ^{1}H N.m.r. studies, one tube per run was sufficient, it was found to be more efficient with regard to machine time to run eight tubes each time for the ^{31}P study, removing them from the oil bath at appropriate intervals and then running the spectra as a batch at room temperature.

Tables and Graphs follow p. 204

^{1}H N.m.r. Studies

Various iminophosphorus materials were prepared for ^{1}H N.m.r. study as discussed on the preceding page. There were three main series considered viz: aliphatic, the dioxaphospholans and dioxaphosphorinans, and finally the oxazacyclic species.

The various results are tabulated in tables 1, 2 and 3 respectively. The main points of note are that

1. the result obtained for the imino-1,2,5-triphenylphosphole were remarkably close to those observed by Cadogan and Scott[9] using G.L.C. techniques.
2. N-(4-methoxy-2-nitrophenyl)-imino-2-phenyl-1,3,2-dioxaphospholan gave a remarkably low rate of reaction. This result was confirmed by ^{31}P N.m.r. study and gives rise to the observation by ^{31}P N.m.r. of the presence of a pentavalent phosphorus species in these decompositions.
3. In accordance with theory as outlined in the introduction to this thesis, six-membered rings generally gave lower rates of reaction than five-membered rings which in turn gave equal or lower rates than four-membered rings.

^{31}P N.m.r. Studies - Thermolysis

A. N-(4-methoxy-2-nitrophenyl)-imino-1,2,5-triphenylphosphole

Thermolysis of the title compound in N.m.r. tubes as discussed at the beginning of this section yielded a rate of formation of the 1,2,5-triphenylphosphole oxide of 7.58 x 10^{-3} mn^{-1}. This result being some 2.5 times faster than that observed by ^{1}H N.m.r. for formation of the 5-methoxy benzofurazan gave further evidence for a pentavalent phosphorus species.

The title material has two charge separations possible across the P-N bond and across the nitro group. On the other hand the pentavalent species suggested for this decomposition has only one - across the nitroxide area. Any solvent system stabilising a less charge separated system would then increase the rate of reaction by preferentially solvating the less charge separated species.

tert-Butylbenzene as used in these observations as solvent is non-polar compared to the bromobenzene used as solvent in the ^{1}H studies (as is d_6-benzene), and so would be expected to give such a result.

Only one product of reaction was observed and despite observation of the ^{31}P N.m.r. spectrum in the region where pentavalent species would be expected, no such absorptions were noted.

B. N-(4-methoxy-2-nitrophenyl)-imino-2-phenyl-1,3,2-dioxaphospholan

Thermolysis of the title compound was performed in a bromobenzene/20% d_6-benzene mixture. The result of 1.63 x 10^{-3} mn^{-1}, being 1.5 times that in the ^1H N.m.r. study suggests, as in A above, an effect by the less polar d_6-benzene on the rate of reaction. The use of bromobenzene as solvent however makes the result much more consistent and comparable with that in the ^1H study.

The first point of note is that several products containing ^{31}P were noted and this indicates that the reaction is presumably complicated by ring opening reactions. The ring closed 2-phenyl-1,3,2-dioxaphospholan oxide was the major product however.

The major result here, however, must be the observation of an absorption at around -54 ppm on the ^{31}P N.m.r. scale. This is exactly where a pentavalent phosphorus species would be expected to absorb and this result is the most direct evidence yet found for the presence of such a species in these decompositions.

What is more, separate studies in this decomposition showed that this result was repeatable and even more importantly that on cooling to room temperature the intensity of the absorption was quite considerable being 0.21 that of the standard used, representing, on the assumption (not too valid) that all intensities can be compared directly, a concentration of around 14% maximum of the total concentration of products and reactants and 20% maximum of the reactant concentration.

The result suggests a remarkably stable pentavalent species, a suggestion confirmed when the same absorption was noted to appear when the reaction mixture was allowed to stand at room temperature for 45 minutes, the intensity being, within experimental error, unchanged.

This result is discussed in greater detail in the final section of this thesis.

^{31}P N.m.r. Studies - Hydrolysis

It was decided to follow the hydrolysis decompositions of the iminophosphines by ^{31}P N.m.r. after observation of the thermolysis result in the case of N-(4-methoxy-2-nitro phenyl)-imino-2-phenyl-1,3,2-dioxaphospholan. The following results were obtained (see also Table 5).

A. N-(4-methoxy-2-nitrophenyl)-imino-1,2,5-triphenylphosphole

The initial result of interest was that observed when the iminophosphine in question was treated with a trace quantity of 1N HCl. Immediate disappearance of the parent species absorption was noted and the appearance of a broad absorption centred at about 26 ppm which moved gradually as the reaction proceeded to 33 ppm. Product absorption was noted at 40 ppm, constant. These figures compare with the parent absorption at 13 ppm.

This result suggests the rapid production of a protonated, charged species which is then solvated by the dioxan used as solvent in these reactions. As reaction proceeds the ratio of solvent to material changes so the solvation will change

and hence the apparent absorption frequency will also vary. This is discussed further in the final section of this thesis.

The actual hydrolysis results were obtained in the spectrometer using a computer programme to take readings at set intervals.

The results of 6.24, 7.27 and 7.4 x 10^{-4} mol l^{-1} mn^{-1} are consistent with each other, and show the reaction as being complete within 2 hours in both cases.

No pentavalent phosphorus species was noted at any time even though the reaction was carried out in the spectrometer. This indicates rapid collapse of any such species even on the ^{31}P N.m.r. time scale.

No other hydrolysis products were observed.

B. N-(4-methyl-2-nitrophenyl)-imino-2-phenyl-1,3,2-dioxaphospholan

Hydrolysis of this material under the same conditions gave several points of note.

Firstly, the rate of reaction, in contrast to the thermolysis case was as fast if not faster than for the iminophosphole, as would be expected from all the introductory discussion to this thesis.

Secondly, several products of hydrolysis are noted, and while the ring closed oxide is the predominant product, three other products were observed, two of which moved markedly across the spectrum as the reaction progressed. Similarly to the protonated iminophosphole postulated above it is surmised that these must be charged species such as

ring opened protonated alcohols which are solvated by the dioxan used as solvent.

Finally, under these hydrolysis conditions, no pentavalent phosphorus species was observed at any time, again indicating that collapse of such a species in this reaction is a rapid affair compared to the ^{31}P N.m.r. time scale in marked contrast to the thermolysis observations already discussed.

Further discussion on these points is made in the closing section of this thesis.

The results of the hydrolysis studies on formation of the ring closed 2-phenyl-1,3,2-dioxaphospholan-2-oxide gave rate constants in the range 6.8-9.7 x 10^{-4} mol l^{-1} mn^{-1}.

C. N-(4-methyl-2-nitrophenyl)-imino-1-phenylphospholan

Hydrolysis of this material under the same conditions gave rate constants for formation of the 1-phenylphospholan-1-oxide of 8.8 x 10^{-4} and 1.18 x 10^{-3} mol l^{-1} mn^{-1}.

No hydrolysis products other than the expected oxide were observed during the reaction although on standing one other peak did appear.

Once again no pentavalent phosphorus species was observed.

Conclusions

The ring effect does not seem particularly marked in these hydrolysis reactions and no concrete theory could be taken from these results as unfortunately the way in which the ^{31}P N.m.r. spectrometer draws out peaks from a series of points the absolute intensity of any peak is open to question.

That no pentavalent species of any sort was observed only serves to underline the remarkable nature of the result obtained in the ^{31}P thermolysis studies.

In-Vacuo Thermolyses of Iminophosphines

In comparison with the decompositions attempted in solution, the decompositions described below were carried out in vacuo in a Kugelröhr vacuum thermolysis apparatus.

The glass sections of the apparatus were dried in the oven overnight and 0.6-1g of material loaded into the base flask. After evacuation of the apparatus the reactant was left in-vacuo for two to three hours to ensure equilibrium before insertion of the glass section into the thermostatically controlled oven, pre-set at 160°.

Interest centered on whether or not any anilines would be produced in the absence of any water and indeed on whether in fact the reaction would proceed in the same fashion at all.

A. Decomposition of N-(4-methoxy-2-nitrophenyl)-imino-2-phenyl-1,3,2-dioxaphospholan

The yellow reactant quickly turned into a reddish oil which on continued heating went black and became solid.

In the distillation flask farthest from the reactant, which in fact was kept at room temperature, a white crystalline solid was deposited while in the middle flask a red oil was collected.

The white crystals were quickly found by i.r. and N.m.r. spectroscopy to be 5-methoxybenzofurazan, the expected volatile decomposition product of the reaction. Yield: 35%.

The red oil, on cooling, gave red crystals (27%) of 4-amino-3-nitroanisole.

This result definitely suggests that a reaction mechanism other than that postulated by Cadogan and Scott[1,2], is responsible here for the production of amines in the decompositions under study.

In the original flask a black tar was noted, this further supporting the theory put forward in the final section of this thesis that a nitrenoid species can be generated in these reactions.

The reaction was also noted to be very rapid in comparison to the solvent reactions studied, presumably the pentavalent species noted in these reactions decomposing rapidly in the absence of any stabilising influence due to solvation.

B. Decomposition of N-(4-methoxy-2-nitrophenyl)-imino-1,2,5-triphenylphosphole

5-Methoxybenzofurazan (15%) was recovered in a flask at room temperature, while 4-amino-3-nitroanisole (20%) was also recovered in this flask. A more interesting result however was the recovery of a red oil giving a ^{31}P N.m.r. absorption at -1.7 ppm. No such species had been observed by ^{31}P N.m.r. in the solution decomposition.

Unfortunately, the oil appeared to contain some 4-amino-3-nitroanisole but i.r. spectroscopy indicated an absorption at 2260 cm^{-1}, where P-H is normally noted. This however is by no means conclusive.

^{1}H N.m.r. gave a mixed spectrum with multiplets centred on 7.4 ppm, 4 ppm and 1.4 ppm. No positive identification was possible from any of these spectra.

On one occasion a suggestion was noted that 1,2,5-triphenylphosphole was a reaction product, as TLC gave a spot showing similar R_f to authentic 1,2,5-triphenylphosphole, and UV light caused fluorescence, a characteristic of the 1,2,5-triphenylphosphole. This evidence however was not conclusive.

Yields were noted to be much lower than in solution chemistry, and that of the amine higher than that of the benzofurazan. Once again support for a different mechanism and this is discussed in the final section.

C. N-(4-methyl-2-nitrophenyl)-imino-1-phenylphospholan

Thermolysis of this material in the Kugelröhr apparatus yielded only 5-methylbenzofurazan (35%) and 4-amino-3-nitro toluene (25%) as products. Once again the presence of an amine as a product indicates a different reaction mechanism from that postulated by Cadogan and Scott[1].

D. N-(4-methyl-2-nitrophenyl)-imino-diethylphenylphosphine

This material gave no reaction in the ^{1}H N.m.r. solvent study but on heating in a Kugelröhr for several hours a very small amount of a crystalline red solid was extracted which gave an i.r. suggestive of an amine.

These results are discussed further in the final section of this thesis.

"Trapping" Experiments

As discussed in the final section of the thesis attempts were made to "trap out" any intermediate present in the decomposition of these materials.

A. N-(4-methoxy-2-nitrophenyl)-imino-1,2,5-triphenylphosphole

The title material was allowed to react with maleic anhydride in a 1:2 ratio in bromobenzene, under nitrogen, under reflux for 3 hours. The reaction mixture was then taken and solvent removed, when the ^{31}P N.m.r. spectrum was run.

Compared to a parent absorption of around 13 ppm, an absorption was noted at 86 ppm. Whereas a pentavalent species would have been expected to absorb at negative ppm, this large positive shift is taken as evidence either that reaction proceeded *via* attack of phosphorus on the oxygen of the maleic anhydride or *else via* a Diels-Alder type of reaction across the phosphole ring. This matter was therefore not pursued further.

B. N-(4-methoxy-2-nitrophenyl)-imino-2-phenyl-1,3,2-dioxaphospholan

The title compound was similarly allowed to react with maleic anhydride and the ^{31}P N.m.r. of the reaction mixture gave a mixture of shifts between 36 and 17 ppm. The parent material gives a shift of 21 ppm and the ring oxide one of around 35 ppm, therefore the result suggests little reaction with the anhydride as an intermediate has been noted in this decomposition at -54 ppm.

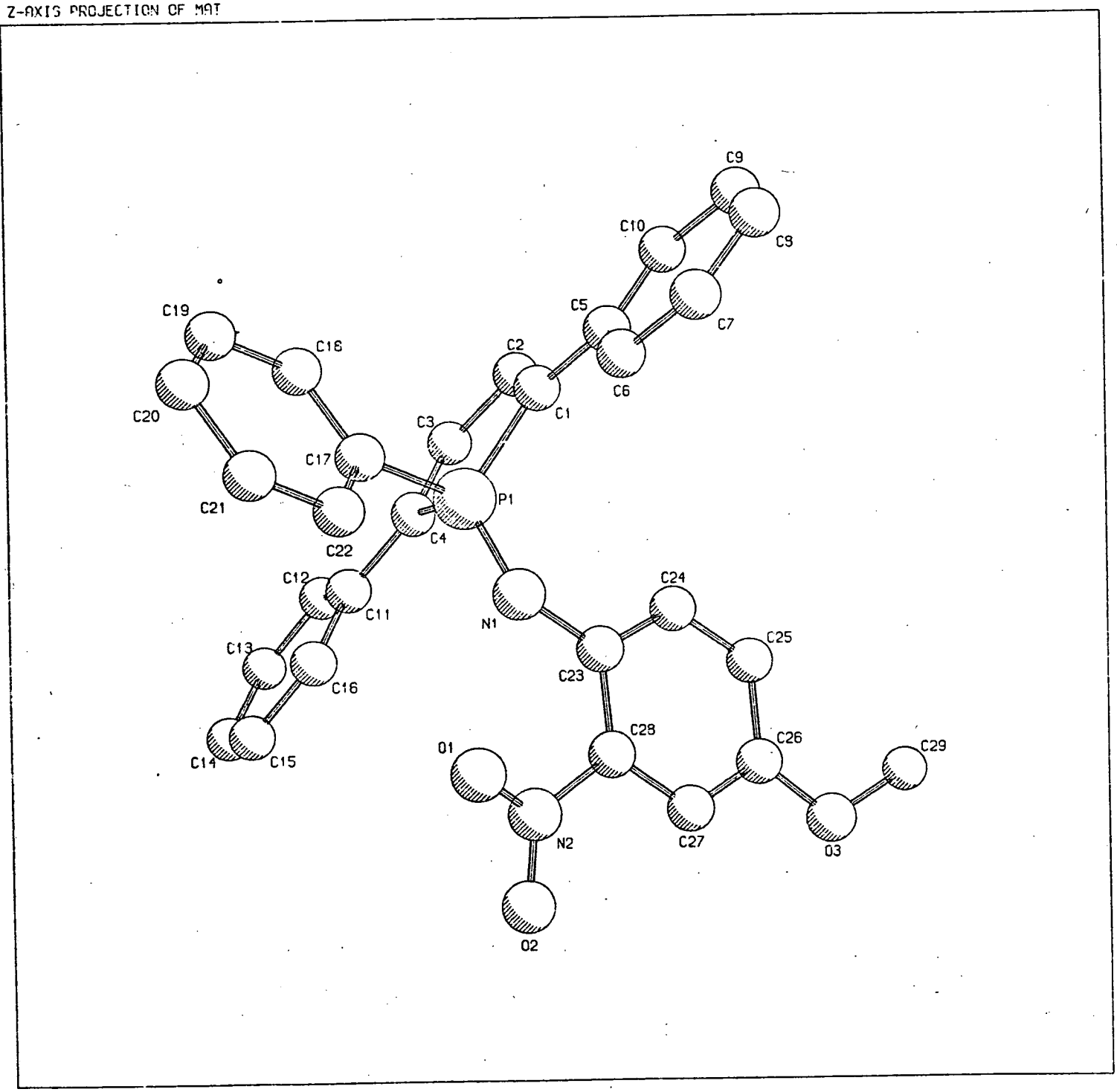
C. N-(4-methoxy-2-nitrophenyl)-imino-1,2,5-triphenylphosphole

As it was possible that the phosphorus had reacted with the oxygen of maleic anhydride, it was decided to attempt the same reaction with cyclohexene. ^{31}P N.m.r. gave shifts of 17.5 ppm and 7.8 ppm, but as the product was an impure mixture no identification was undertaken.

D. N-(4-methoxy-2-nitrophenyl)-imino-2-phenyl-1,3,2-dioxaphospholan

No reaction was noted with cyclohexene and ^{31}P N.m.r. gave shifts at 36 ppm as would be expected.

Z-AXIS PROJECTION OF MAT



E. Crystal structure of N-(4-methoxy-2-nitrophenyl)-imino-1,2,5-triphenylphosphole

The crystal structure of the title compound was determined by Dr. L. Jones and Dr. R.O. Gould of this department. The Z projection is shown opposite.

Table of selected bond lengths and angles

Bond	Bond length (Å)	Bond angles(°)
P_1-N_1	1.557 (4)	$C_4P_1C_1$ = 94.0(3)
N_1-C_{23}	1.375 (7)	
N_2-C_{28}	1.448 (9)	$N_1P_1C_{17}$ = 107.0(3)
P_1-C_1	1.803 (6)	$P_1N_1C_{23}$ = 127.2(5)
P_1-C_4	1.807 (6)	
C_2-C_3	1.450 (8)	
C_1-C_2	1.345(10)	
C_3-C_4	1.339 (9)	

It is evident from the projection that the phosphorus atom is tetrahedrally co-ordinated. The bond angle $N_1P_1C_{17}$ is indeed fairly close to the expected value of 109.5°. However the bond angle $C_4P_1C_1$ of the phosphole ring, at 94.0° is in fact much closer to the 90° angle, which phosphorus accommodates easily in the penta-co-ordinate state, than the tetrahedral value required here. There must, therefore, be a considerable amount of angle strain present in the phosphole ring when the phosphorus atom is quadruply co-ordinated.

The bond angle $P_1N_1C_{23}$ suggests that the nitrogen atom is sp^2 hybridised, with some distortion of the angle occurring, possibly due to some interference due to the ortho-nitro-group on the aryl ring.

However, the length of the P_1-N_1 bond is of some interest. The P-N double bond length calculated from covalent radii is 1.64Å,[34] but the bond length found here is significantly shorter.

It has been shown[35] that a phosphorus atom in a strained ring has an enhanced positive nature, in analogy with alicyclic ketones,[36,37] and this has been attributed to lowered occupation of the phosphorus 3d orbitals. The shortened P-N distance observed may thus be due to d^{π}-p^{π} overlap between the phosphorus and the nitrogen. The greatest such overlap would occur if the nitrogen was sp hybridised and the increase in the bond angle $P_1N_1C_{23}$ may be due to some contribution of this nature, although the reluctance of phosphorus to enter into π bonds is well established.

DISCUSSION

The Ring Effect (1)

Having decided on the ^{1}H and ^{31}P N.m.r. approach to measuring the kinetics of the reaction involved in the decomposition of cyclic phosphinimines the method had to be tested against the results obtained by Cadogan and Scott[1] as a check of its reliability.

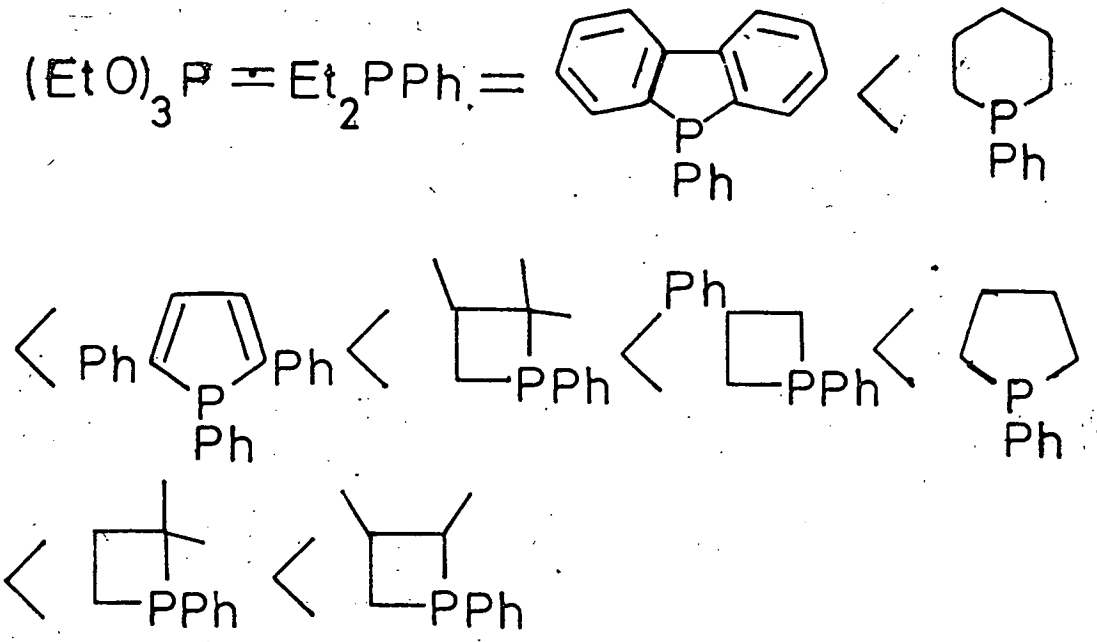
As N-(4-methoxy-2-nitrophenyl)-imino-1,2,5-triphenyl-phosphole had been found to be a readily prepared and crystalline material[1] this was taken for comparative purposes.

It was firstly demonstrated that the absorptions of the methoxyl group of reactant and product appeared at sufficiently separate shifts. The standard was then run twice and the rate of reaction (first-order) measured. The result of 3×10^{-3} mn^{-1}, obtained by the N.m.r. method, was, considering the errors inherent in this method and that of Cadogan and Scott, remarkably close to that previously reported. The difference of 6.6% being well within experimental error.

It was therefore decided to proceed with this method and the results obtained for the series of cyclic and acyclic phosphinimines synthesised are shown in Table 1 (following p.204).

The Aliphatic Series

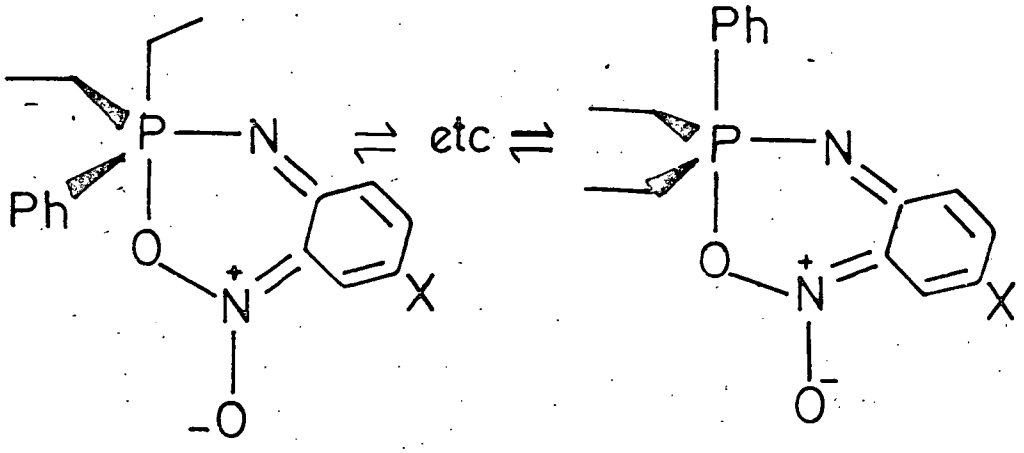
The results obtained for the alicyclic series were as follows:



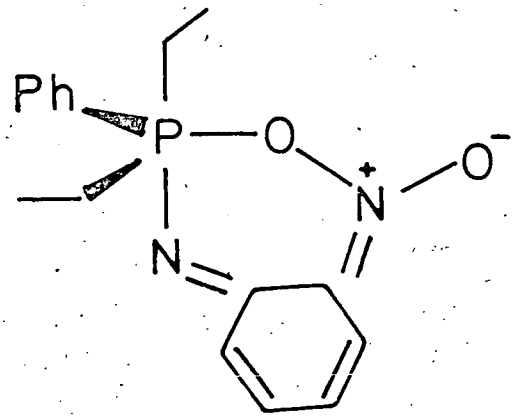
where > signifies a difference in rate.

While basically following the pattern one might expect from such a series after all the preceding discussions on ring strain effects, there are certain anomalies which require explanation. The following discussion attempts to rationalise these anomalies; and evidence gained from studies on other species and theories derived from work discussed in the introduction to this thesis will be used to show a logical, consistent sequence of rate of reaction.

That diethylphenylphosphinimine should give a zero rate is expected from all previous discussions as, having no internal strain from annular considerations there is no, or insufficient, driving force in terms of energy release for decomposition to occur. The two ethyl groups could take either an apical or equatorial position in the five co-ordinate intermediate species as shown as follows -



As the preference of oxygen atoms for the apical sites and the leaning of nitrogen to occupation of equatorial sites, due to the availability of p_π-d_π back-bonding, has already been discussed (p.20 and 21 respectively) it would seem likely that rotation to forms such as 116 below would be energetically less likely.



(116)

Following similar arguments to those used to explain the differences in the rates of substitution of substituted benzenoid derivatives it could in fact be considered likely that, apart from being just a reaction without sufficient driving force, the position is that there are certain extra

energy barriers to be overcome in setting up five co-ordinate species with this particular kind of co-ordinated atom arrangement due to the higher energy of certain of the canonical forms. In that case, without some other influence, such as relief of annular strain, to overcome this barrier, such a reaction would be disfavoured in comparison to some others.

Similar arguments can be put forward for the case where the phosphorus moiety is triphenylphosphine or triethylphosphite, although in the latter a very stable penta co-ordinated species could be generated and lack of reaction would appear to indicate the power of ring strain relief in these decompositions.

The relief of ring strain must be judged against the relative stabilities of any possible intermediates or transition states that may be formed in the reaction, however.

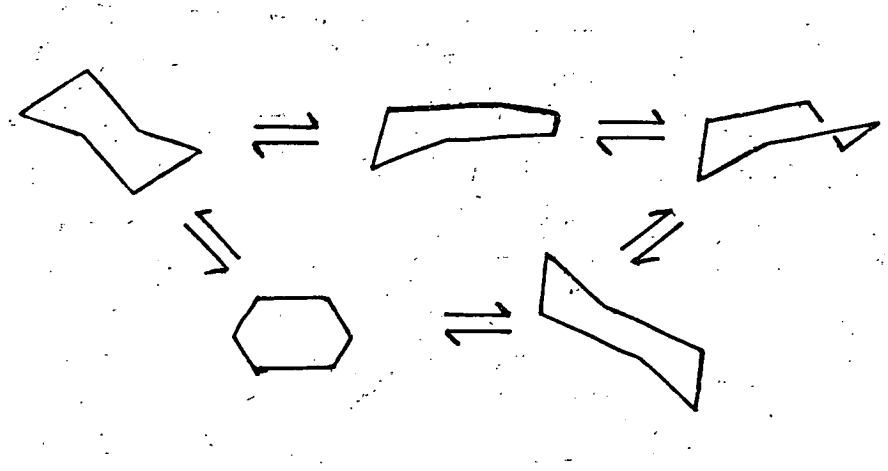
In the series discussed above the relative effect of the oxygen and nitrogen atoms on any of the transition states should be the same and so rates of reaction differences can be attributed to some effect of the cyclic phosphole moiety.

We have seen that the open-chain moiety gives no reaction and that the phosphole moiety gives decomposition at $3.0\text{-}3.3 \times 10^{-3}$ mn^{-1} in a first-order reaction. The phosphole moiety has the same number of carbon atoms in the ring as the open-chain moiety has over the two ethyl groups. It would appear therefore that the presence of a ring has a marked effect, as any differences in inductive effects due to the presence of the phenyl groups on the phosphole ring would seem unlikely to generate a difference in rate as remarkable as this.

The six-membered ring phosphorinan moiety gave slower decomposition, as one would expect, than the phosphole moiety. However, should one expect decomposition at all?

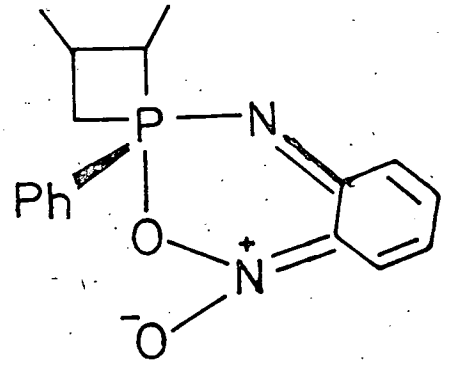
It has been shown in previous discussion (p.9) that the six-membered ring can easily span either an apical/equatorial or diequatorial position. The question lies more in the source of the ring strain that overcomes the transition energy.

It is widely known that the six-membered ring exists as interchanging boat and chair forms with various intermediate stages, viz:



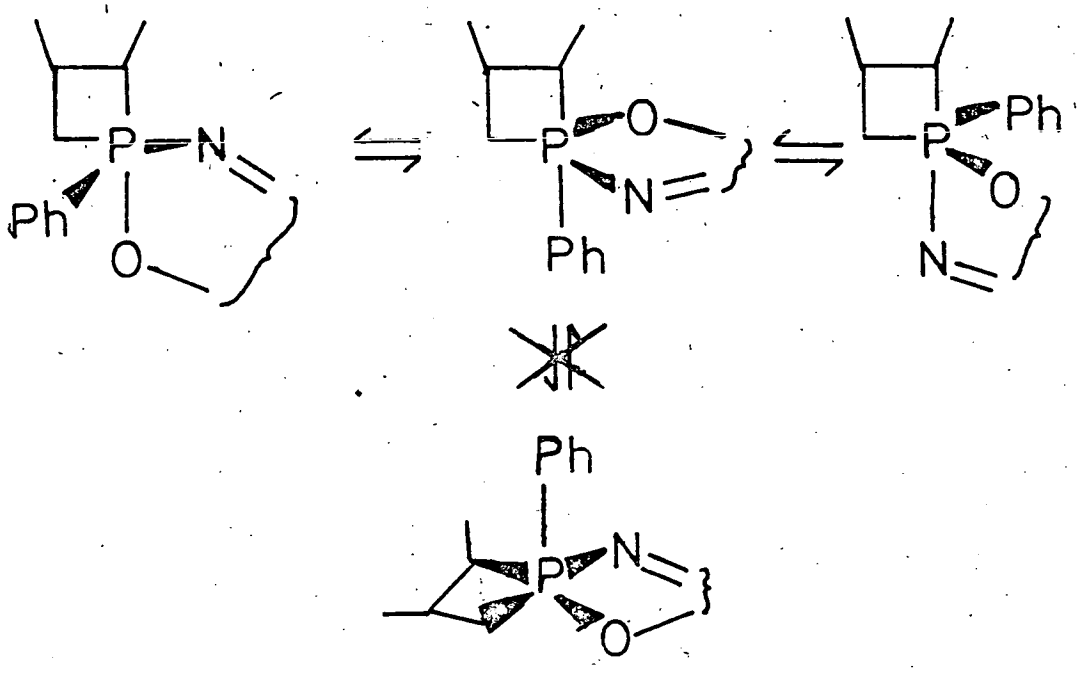
While the chair form has inherently little strain, the various other forms lead to some varying degrees of hydrogen/hydrogen interaction and angle deformation strain. This then is the source of ring strain in the phosphorinan ring. However, the much greater rate of reaction due to the phosphole moiety arises because of the angle constraint at the phosphorus atom in the five-membered ring. This constraint has a much more important effect than any hydrogen-hydrogen effects, as is well known in carbon chemistry and hence the relative rates of reaction. That the rate then found for the four-

membered rings is greater requires little explanation other than that as a 90° angle exists at phosphorus already, little energy is required to move to the penta-co-ordinate state with the ring apical/equatorial, viz:

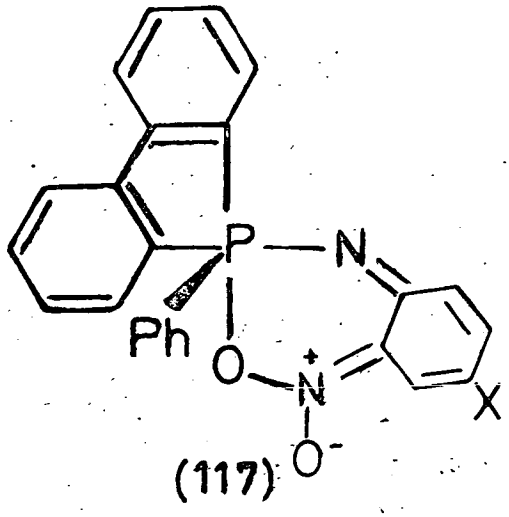


A rapid rate would then be expected as the transition energy to be overcome (i.e. oxygen attack at phosphorus giving angle change at phosphorus) is low.

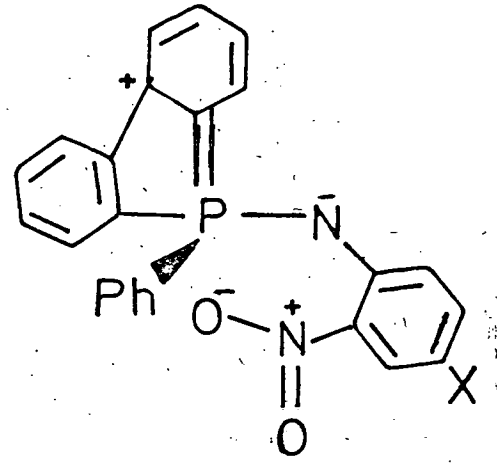
With these particular transition species or intermediates, it is interesting to note that the four-membered phosphetan ring is very unlikely to rotate to a diequatorial position so that in this instance the phosphetan ring is likely to act as a pivot while the other three co-ordinated atoms rotate around phosphorus, viz:



Following similar arguments as put forward for the diethylphenylphosphinimine case, there would appear to be no inherent energy gain in the triphenylphosphinimine case and so no surprise is engendered by the zero rate here. On the other hand, the zero rate noted in the case of the 9-phenyl-9-phosphafluorene case at first sight appears odd, as one would expect something similar to the 1,2,5-triphenylphosphinimine result. On further consideration however, it can be seen that in the 9-phenyl-9-phosphafluorene case, on attaining a penta-co-ordinate arrangement (117), an angle of 90° at phosphorus would place a great deal of strain at the angle at the α-carbon atoms as the phosphafluorene structure is held strictly planar by the "side-structure" rings and so an overall increase in annular strain may even occur.



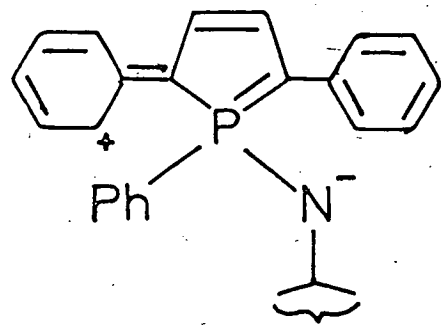
(117)



(118)

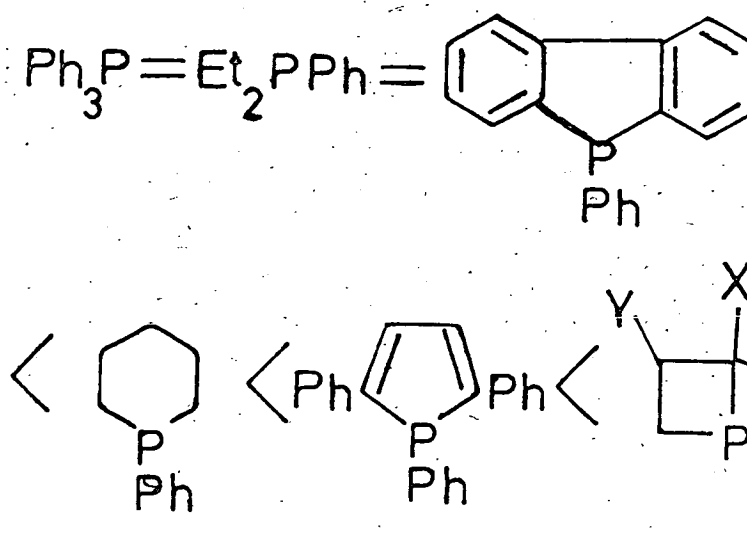
Some reduction in reactivity of such a species may also be attributable to resonance forms such as 118 leading to reduced incentive for nucleophilic attack by oxygen at the phosphorus atom.

While several similar structures such as



can be written in the 1,2,5-triphenylphosphole moiety case, many more can be written for the 9-phenyl-9-phosphafluorene example and so the "charge" on phosphorus may be even more diffuse than normal. Resonance such as this is also much less likely into a straight phenyl group than the "side-structure" rings of the phosphafluorene.

So far then we have a rationale for the following general series:



The results requiring further discussion therefore are the relative rates of 1-phenylphospholanimine and the phosphole case, the variations amongst the phosphetan series itself, and finally the relative rates of the phosphetans to the 1-phenyl-phospholanimine.

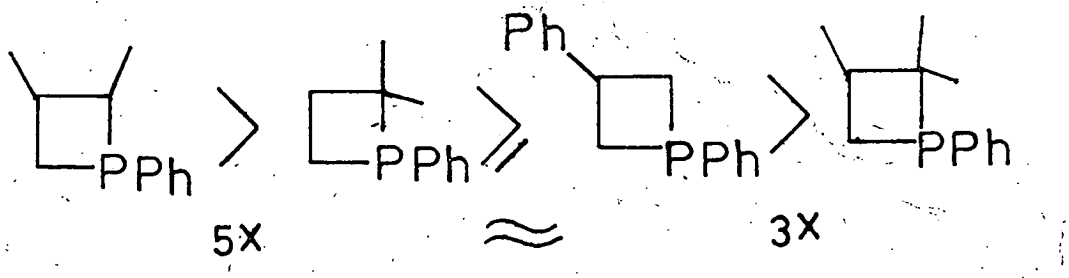
1-Phenylphospholan relative to 1,2,5-triphenylphosphole

Firstly, compare the 1-phenylphospholanimine result with that of the 1,2,5-triphenylphosphole moiety. Why a difference of between 6 and 8 times the rate?

While some increase might be expected due to lack of steric factors such as the phenyl groups on the phosphole ring, X-ray crystallographic studies on the phosphole case (p.132) have shown that the phenyl groups on the phosphole ring are spatially orientated so as to show no apparent hindrance to SN1 nucleophilic attack by oxygen at the phosphorus atom (see z-axis projection facing p.132). That the 1-phenylphospholan moiety gives such a faster reaction would therefore seem to lie firmly in the lack of unsaturation in the ring, as when the phosphole ring enters the penta co-ordinate arrangement, the 90^{o} angle at phosphorus must place large angle strain on the other angles in the ring which due to unsaturation are held spatially more planar while the unsaturated ring can flex to accommodate the additional strain. The phospholan ring could therefore be expected to alleviate ring strain more effectively than the phosphole ring and hence the difference in rate. This then is consistent with the zero rate of the 9-phenyl-9-phosphafluorene moiety 117 where the ring is held completely planar and also the results of Haake et al.[88] where a double bond conjugated with phosphorus decreased the rate of reaction in the hydrolysis of a series of cyclic 5-membered phosphinic esters.

The Phosphetan Series

Considering then the relative rates of decomposition of the substituted phosphetan series. This can be seen to be as follows:

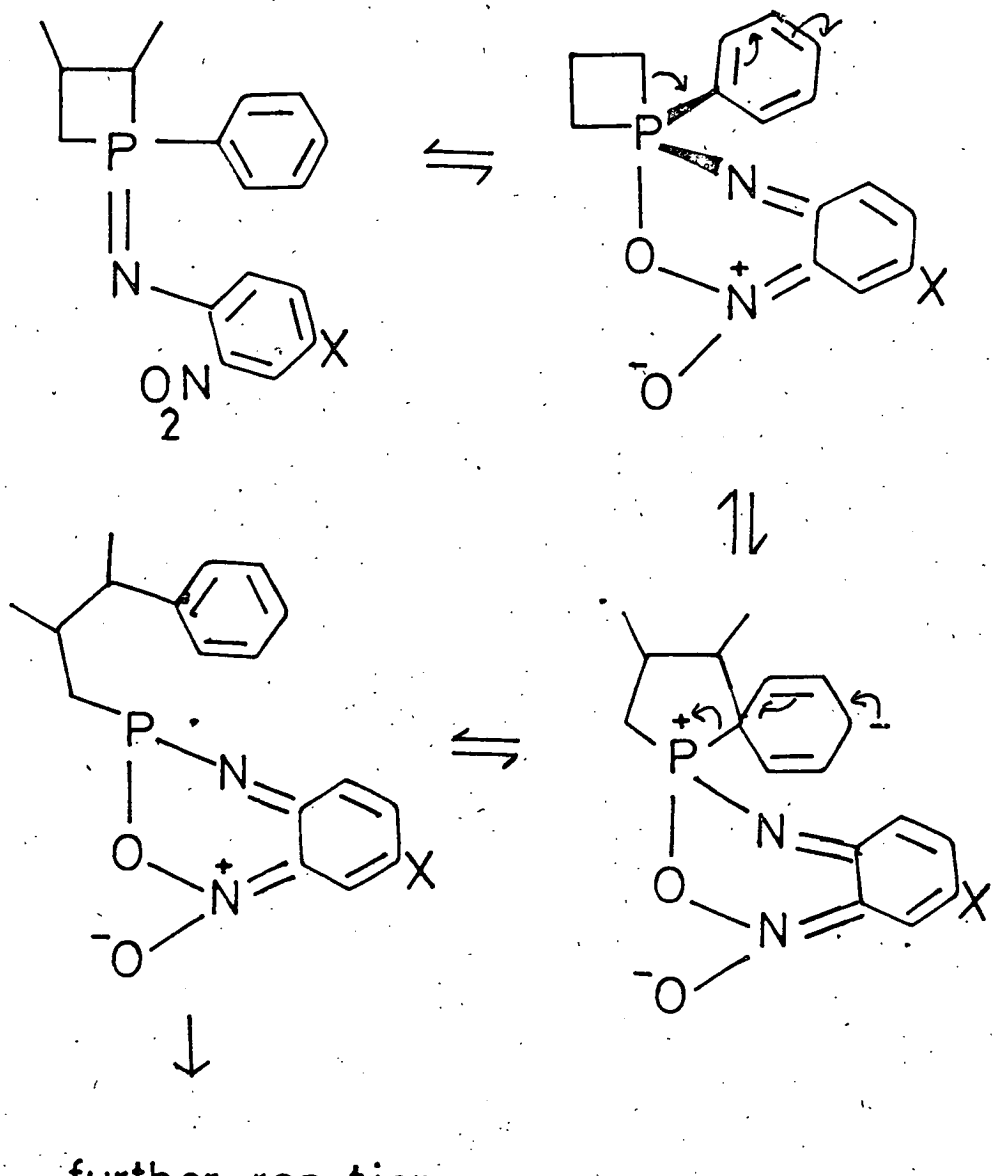


Either the 2,3-dimethyl- case has a factor causing stabilisation of the penta co-ordinate intermediate or the others have some factor stabilising the original form of the imine.

Hawes and Trippett[84] have commented on the retardation of the hydrolysis reaction of ∝-substituted phosphetans to give an apparently "normal" rate of reaction. Whereas steric hindrance in the phosphole case has been discounted the smaller, much more spatially compact phosphetans appear to give steric involvement of ∝-groups. However, the retardation seen by Hawes and Trippett on this occasion was much more marked for tetra-∝-substitution by methyl groups rather than the bisubstitution evident here, and they saw little to suggest one $\geq C(Me)_2$ grouping would greatly affect the rate.

A complication in considering ring effects in phosphetan reactions is the possibility of ring opening[48,49,50] reactions during SN2 reactions at phosphorus. Here we have the

possibility of ring opening, then, leading to either an open-chain species or a five-membered ring species, viz:



SCHEME 32

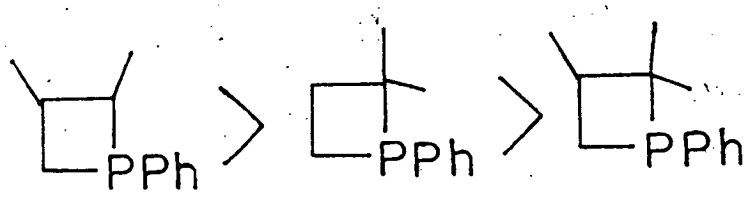
Such side reactions would then reduce the concentration of penta co-ordinated species present in solution and as the current series of reactions under discussion are first-order reactions and it is effectively being claimed that the rate

determining step is the formation of such an intermediate any reduction in its concentration would be to give an apparent reduction in the rate of reaction seen by considering the rate of formation of one decomposition product, i.e. 5-substituted-benzofurazan. Consideration of the series of phosphetans used in these decompositions however suggests that each is as likely as the other to undergo ring expansions or ring opening reactions, particularly as each phosphetan has one CMe_2 or CH_2 group capable of making such ring rearrangements. While Fishwick and Flint[182] have performed some studies on the relative predominances of such migrations and the more likely is migration of $-\bar{C}H_2$ compared to $\bar{C}Me_2$, presumably due to the relative stabilities of the respective anions, both can occur, and in the series above there is little to indicate that this would have much effect on the relative rates of reaction.

This then tends to suggest that there is some steric factor here and while Hawes and Trippett[84] were concerned with a rate reduction of some 4×10^3, here the single CMe_2 group α- to phosphorus gives a rate reduction of 5 to 15 and Hawes and Trippett do suggest that one CMe_2 group would only have such an effect.

A further point here is that substitution in the 3-position is known to stabilise 4-membered phosphetan rings.[174] A rationale can therefore be made that with only one α-methyl group the 2,3-dimethyl case should react most rapidly while the 2,2-dimethyl case should be more sterically inhibited and the 2,2,3-trimethyl case should be sterically inhibited and

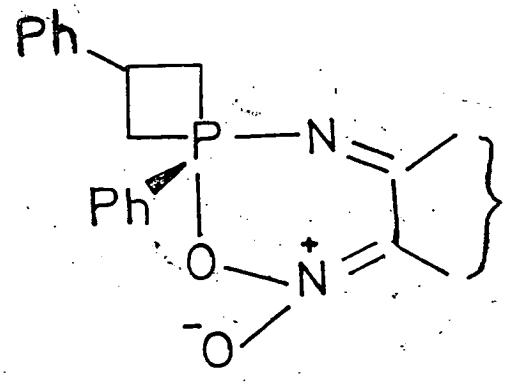
stabilised by the 3-substitution, hence a relative rate pattern as seen, viz:



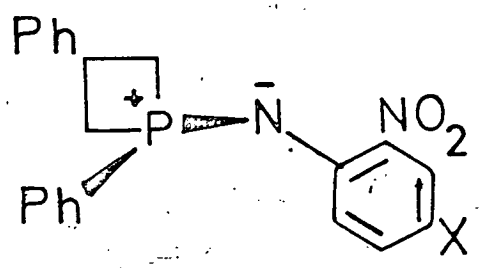
This series taking account of the theory that the steric hindrance due to α-methyl groups is likely to be more relevant in this series than stabilisation at the 3-position by methyl groups.

Finally, this leaves the relative rate of the 1,3-diphenyl substituted phosphetan to be considered. As this particular species has no α-methyl groups, following the arguments above this particular example would have been expected to give a rate of reaction at least as fast as the 2,3-dimethyl analogue. The phenyl group in the 3-position must, at first sight, therefore have either a de-stabilising effect on the initial phosphetan or a stabilising effect on the intermediate or penta co-ordinate transition species.

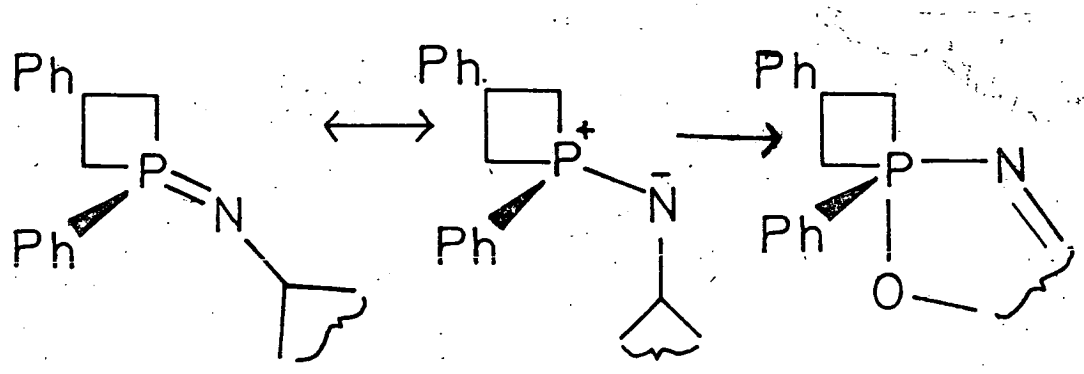
No obvious stabilisation, of the intermediate or transition species, can be deduced from consideration of



which would be due to the phenyl group in the 3-position alone. Furthermore on consideration of the reactant in the form



some stabilisation of $P^{\delta+}$ could be envisaged by induction from methyl groups known to be electron pushers but as a phenyl group is a known electron sink this would seem to suggest this particular moiety should indeed give a high rate of reaction as the formation of a penta co-ordinate species will alleviate this de-stabilisation by removing the partial positive charge that can be envisaged on phosphorus, viz:



The relatively slow rate of reaction in this case therefore may well revolve around the result found for the 2-phenyl-1,3,2-dioxaphospholan moiety (see p.152) where the penta co-ordinate species involved in the reaction would appear to have a definite life-time. Here there appears to be no reason why the reaction rate found should be lower than that

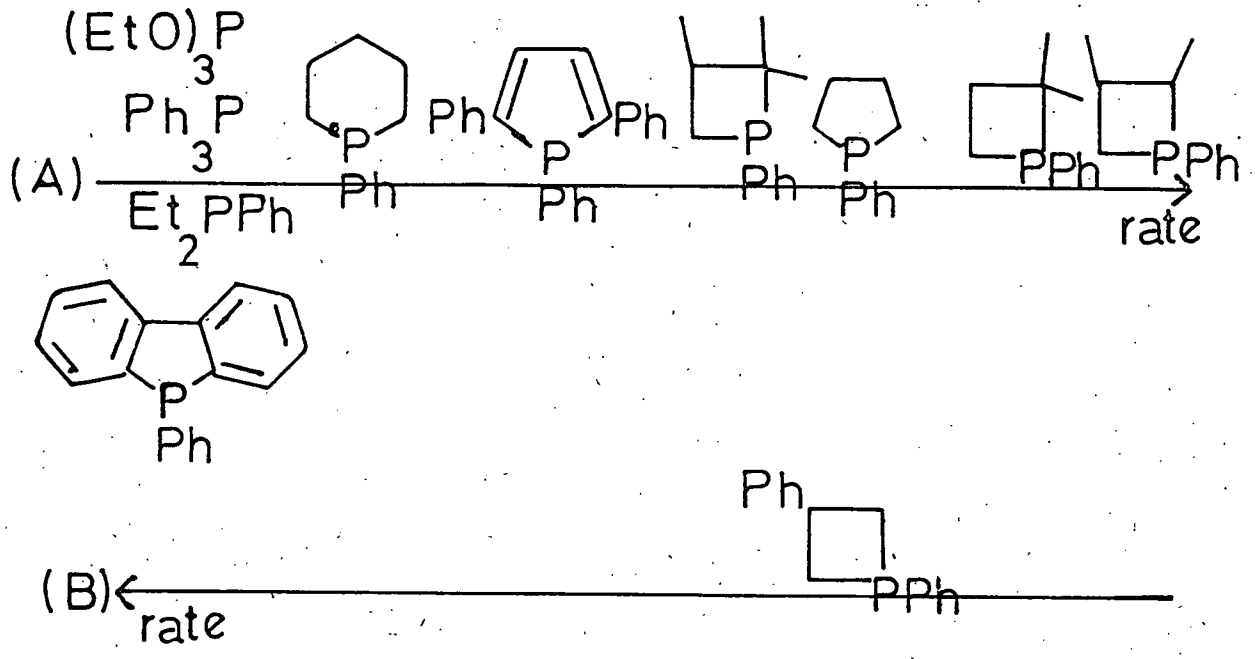
for the 2,3-dimethyl substituted case. There are no apparent steric factors to inhibit the reaction, and there are some electronic reasons why the penta co-ordinate species should be favoured. It is therefore suggested that this particular decomposition may to some extent be governed by the stability of the penta co-ordinate species involved and to some extent by ring expansion reactions as in this case there are two CH_2 groups α to the phosphorus atom which can give preferential ring expansion compared to the CHMe and CMe_2 groups of the other phosphetans studied.

Imino-1-phenylphospholan compared to the Phosphetan Series

Initially it would have been assumed that all the four-membered ring phosphetans studied should give a rate of reaction higher than that observed for the imino-1-phenyl-phospholan. That the phosphetans give a varied set of results compared to the phospholan studied would seem to confirm the relative influences of steric factors, stability of the transition state or intermediate species and relief of ring strain - all factors having to be considered before rationalising the series.

Relative Rates of Reaction - Aliphatic Series

From these discussions it would now appear that when written as follows the aliphatic series studied has given a logical, consistent set of data based on the concept of the involvement of a penta co-ordinated species, viz:

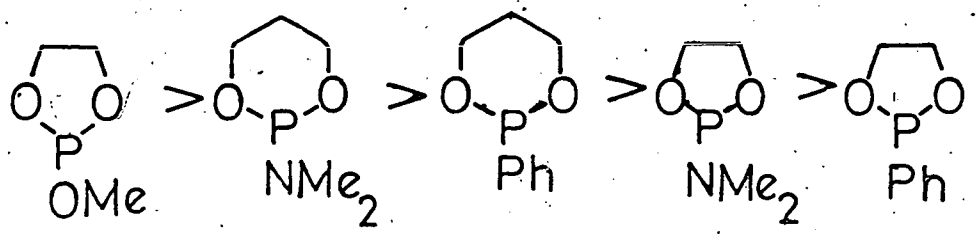


(A) rate increases due to relief of strain

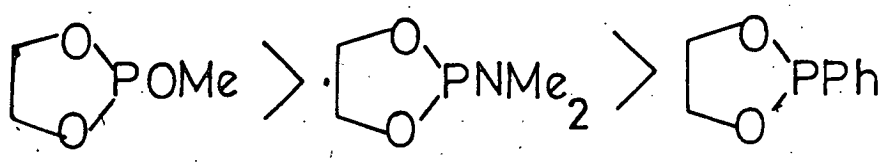
(B) rate decreases due to stability of rn intermediate

The Dioxaphospholan/Dioxaphosphorinan Series

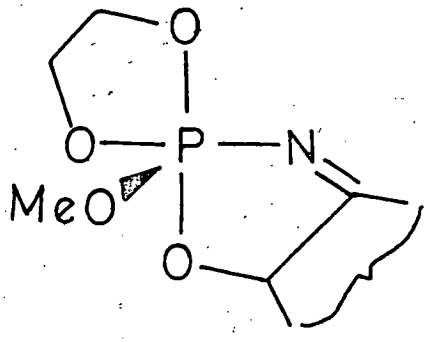
Considering initially the series within itself and not in comparison to the aliphatic series we have relative rates of reaction as follows:



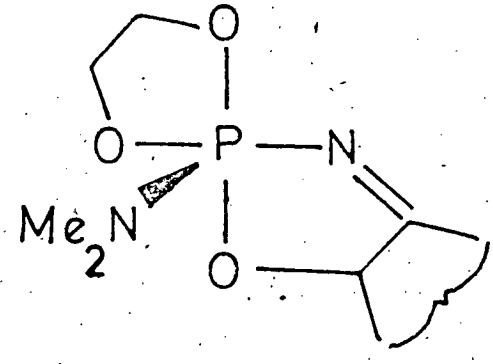
At first sight this series of reaction rates appears to follow no obvious pattern. Consider the five-membered ring sequence itself, however, viz:



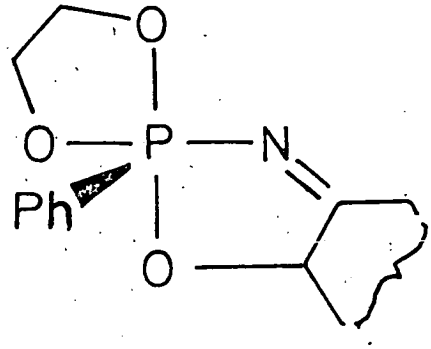
On forming the postulated penta co-ordinate transition species or intermediates the following would be postulated



(119)



(120)



(121)

In view of the apicophilicity of the various substituents on phosphorus in the parent phosphines, the most stable species expected would be that formed from the 2-methoxy-1,3,2-dioxaphospholan (119) as in this penta co-ordinate species any of

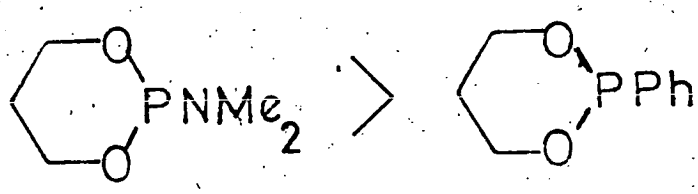
the five co-ordinated atoms will take up apical positions without any major restriction of any "rotation" within the species.

In that penta co-ordinate species derived from the imino-N-dimethyl-1,3,2-dioxaphospholan (120) the presence of two co-ordinated nitrogen atoms would indicate a relative restriction in energy terms to the favourability of certain rotations compared to the previous case as the nitrogen atoms would "prefer" to remain equatorially co-ordinated.

Finally, the even lower apicophilicity of the phenyl group in the last case would suggest that energetically several rotations are disfavoured compared to both the other species, so as not to place the phenyl group apically.

The relative stabilities of the relevant penta co-ordinate species are therefore in line with the observed comparative rates of reaction for these species.

Similarly, on consideration of the six-membered substituted dioxaphosphorinans a logical sequence is observed, viz:



What is surprising however is the relative rates between the six- and five-membered ring species.

That the six-membered ring species gave higher rates of reaction than two of the five-membered species seems to be contrary to the theories put forward so far.

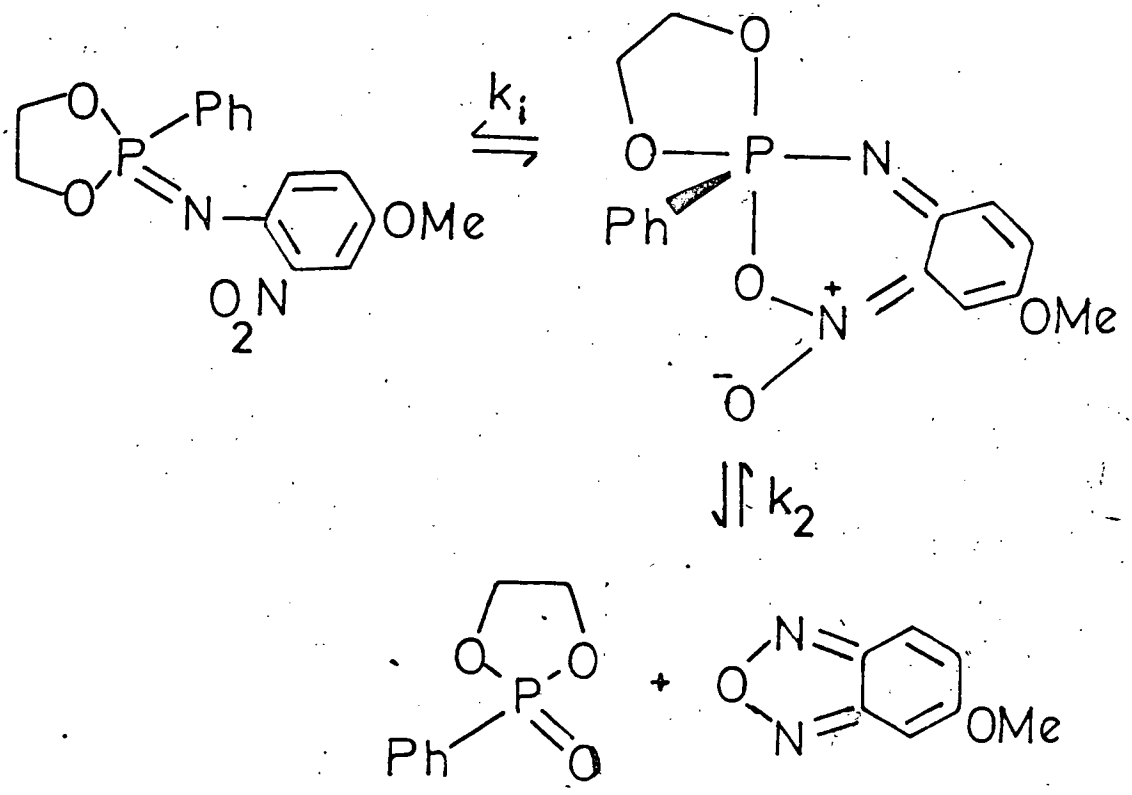
The result obtained in the ^{31}P N.m.r. observations of the decomposition of N-(4-methyl-2-nitrophenyl)-imino-2-phenyl-1,3,2-dioxaphospholan must now be considered.

On running the reaction in a sealed tube under the usual conditions, and observing the ^{31}P N.m.r. spectrum at various intervals, an absorption was noted at -54 ppm - exactly in the region where penta co-ordinate species are known to absorb.[167] This absorption achieved an intensity of around 20 per cent of the reactant absorption on occasions.

This direct evidence of a penta co-ordinate species having a distinct life-time leads to a logical rationalisation of the series shown above.

In the penta co-ordinate species formed the five-membered ring moieties gain extensive release of ring strain. Furthermore, following a host of examples in the chemical literature, the penta co-ordinate species formed has a high number of apicophilic ligands so forming a very stable species.

The evidence here from the ^{31}P N.m.r. result and the relevant rate data would appear to suggest that the five-membered ring moieties form relatively stable penta co-ordinate species and that while in the decompositions discussed previously the rate determining step was taken to be the formation of a penta co-ordinate species, these particular reactions would therefore appear to have relatively much more significant rates of decomposition of the penta co-ordinate species, i.e. in the reaction



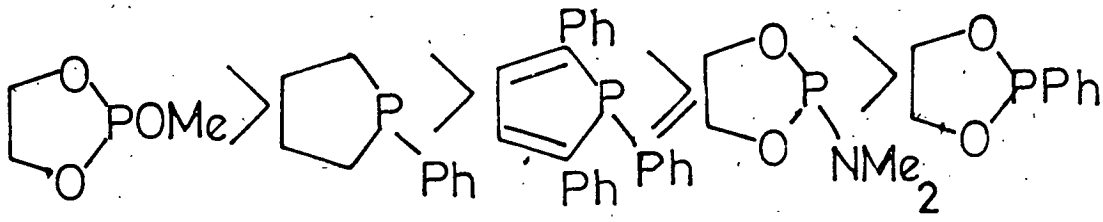
SCHEME 33

k_2 is relatively more significant than in the similar aliphatic series where k_1 is completely dominant.

In the six-membered ring series, the relief of ring strain is not nearly so marked and the relative stability of the penta co-ordinate species therefore not so relevant, and this factor is not observed in the relative rates of these molecules. The situation therefore is one of competing stability of the penta co-ordinate species with relief of ring strain giving the observed rates.

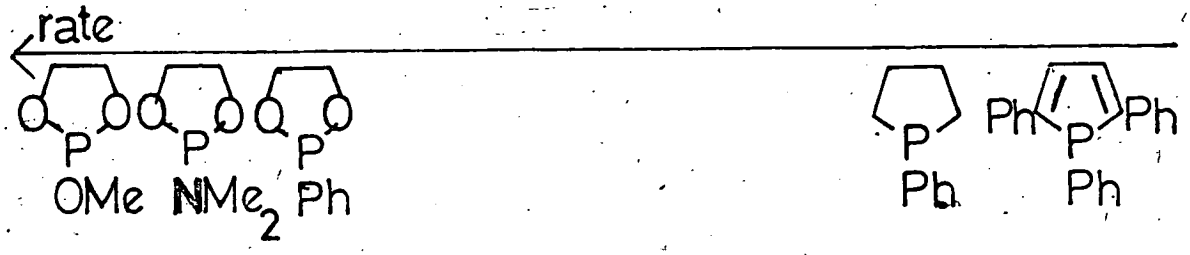
Comparison of the Alicyclic Series with the Oxycyclic Series

The effect of the stability of the penta co-ordinate species in the case of the five-membered cyclic oxyphosphinimines is more obviously noted on comparison with the alicyclic series. In terms of five-membered rings the series becomes:

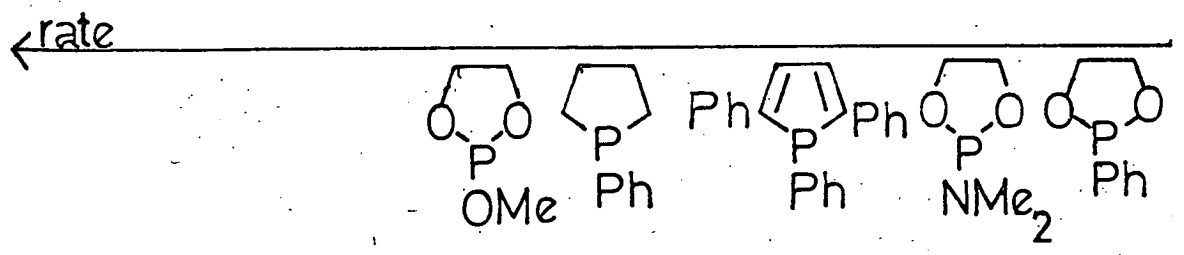


Following the idea that the formation of a stable penta co-ordinated species from the imine, with relief of ring strain, should give a rapid reaction, all the preceding discussions would have suggested that the oxycyclic species should have given much higher observed rates of reaction than for the alicyclic cases. That this is not the case is apparent. The 2-methoxy-1,3,2-dioxaphospholan material gave a rate only 1.5-2.0 times that of the 1-phenylphospholan case while the others gave rates lower even than the 1,2,5-triphenylphosphole moiety.

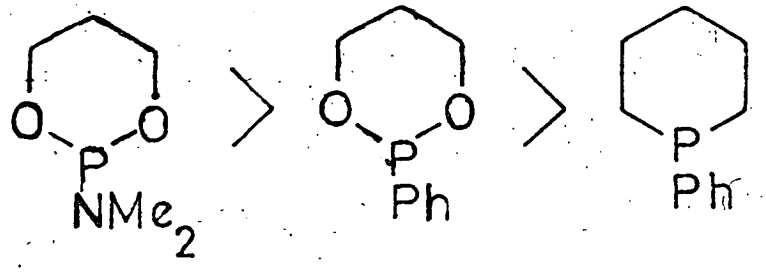
Given the arguments discussed in the section above with regard to the stability of the penta co-ordinate species involved in the oxycyclic cases it can be seen that the rates observed for the oxycyclic series have been considerably reduced and that rather than



we have the observed



It is of interest also to compare the six-membered ring results, viz:



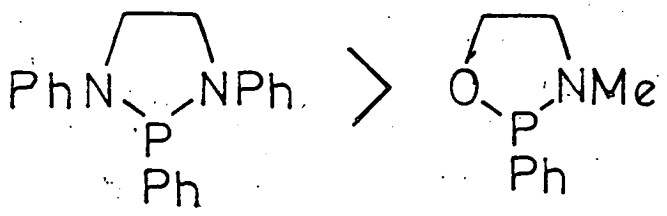
This series is consistent with all the arguments put forward above,

i.e. (a) P-NMe_2 gives a higher rate of reaction than P-Ph

(b) Oxycyclic species give a higher rate than alicyclic species but that the increase in rate is not as marked as might be expected.

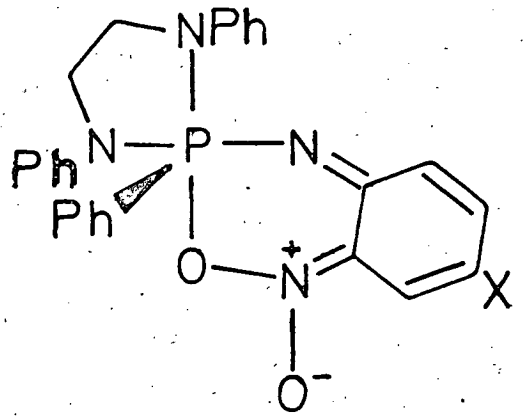
The Oxazacyclic and Diazacyclic Series

Only two materials have been studied in this series, viz:

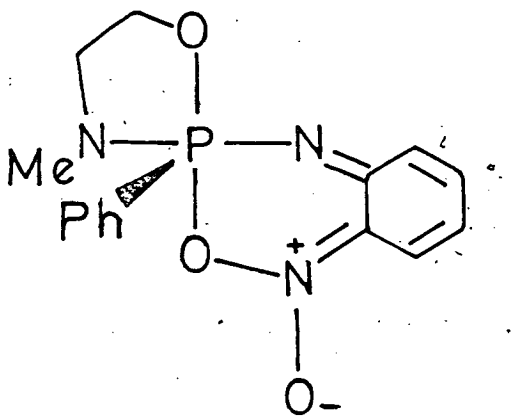


(122) (123)

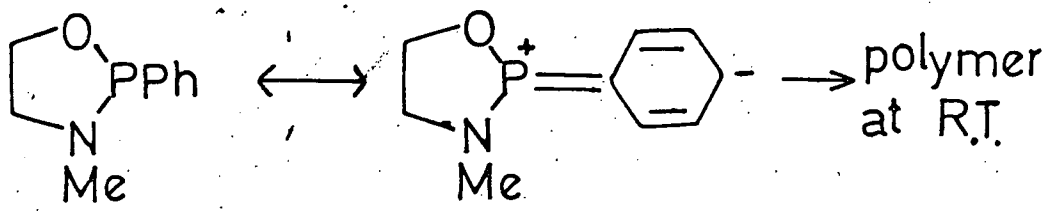
As on formation of the relevant penta co-ordinate species the imine of 1,2,3-triphenyldiazaphosphole (122), should have to form a species of the form



with at least one nitrogen apical, whereas the imine of 3-methyl-2-phenyl-1,3,2-oxazaphospholan (123) could form a species such as

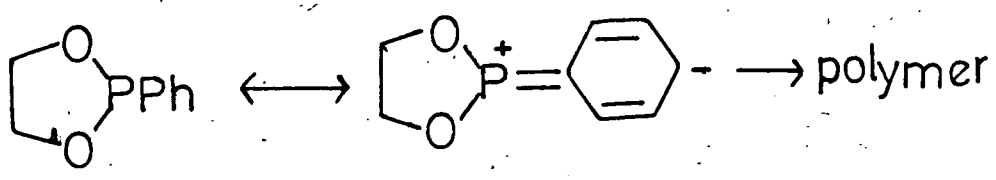


with two oxygen atoms apical, it would have appeared that these rates should have been reversed. Furthermore, Greenhalgh, Newbery, Woodcock and Hudson[183] have found that 3-methyl-2-phenyl-1,3,2-oxazaphospholan reacts much faster than the 2-methoxy analogue in reaction with isocyanate due to an increase in the inherent ring strain in the former due to contributions from such as



Following arguments similar to those for the imine of 1,3-diphenylphosphetan however, a case can be made out that in the imine a de-stabilisation (or increase in energy) of the reactant allows for an easier (lower energy delta) transition to the penta co-ordinate species. That this species has relieved the extra strain is obvious as no charge is extant on the phosphorus in this species and as the penta co-ordinate species is stabilised by having two oxygen atoms apically located this extra stability may account for the lower rate of reaction observed.

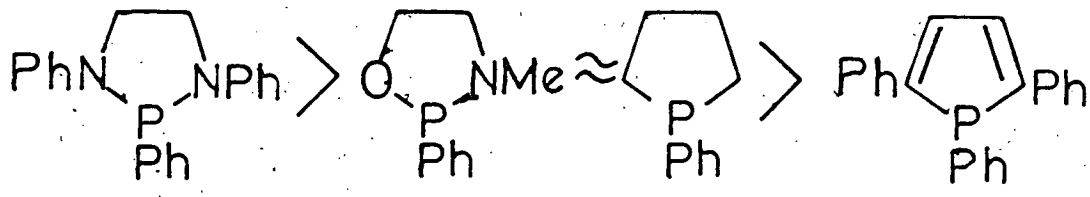
It is interesting to note here that 2-phenyl-1,3,2-dioxaphospholan also polymerises at room temperature[183] also due to species such as



That this imine, as well as the 1,3-diphenylphosphetan and 3-methyl-2-phenyl-1,3,2-oxazaphospholan species all give lower rates of decomposition seems to lend consistency to these arguments above.

Alicyclic Series compared to the Oxazacyclic and Diazacyclic Series

The comparison in rates of decomposition is seen to be

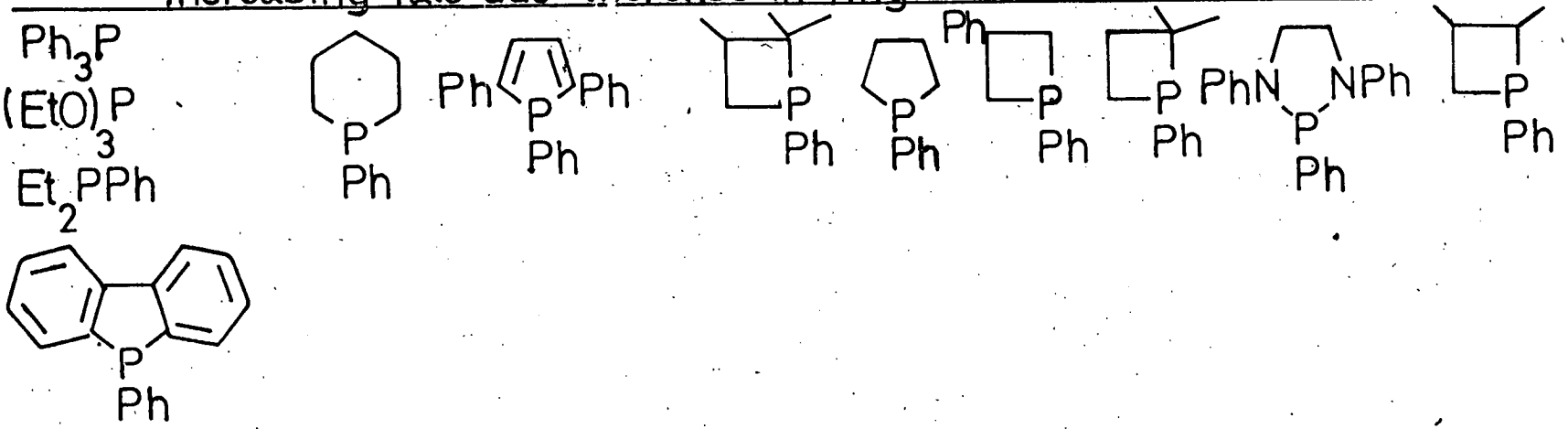


although none of the differences are extremely great, the rates for the oxy and aza substituted rings presumably being reduced due to the added stability of the oxazaphospholan ring in the penta co-ordinate species and of the decrease in stability of the penta co-ordinate species in the diazaphosphole case due to the presence of apical nitrogens.

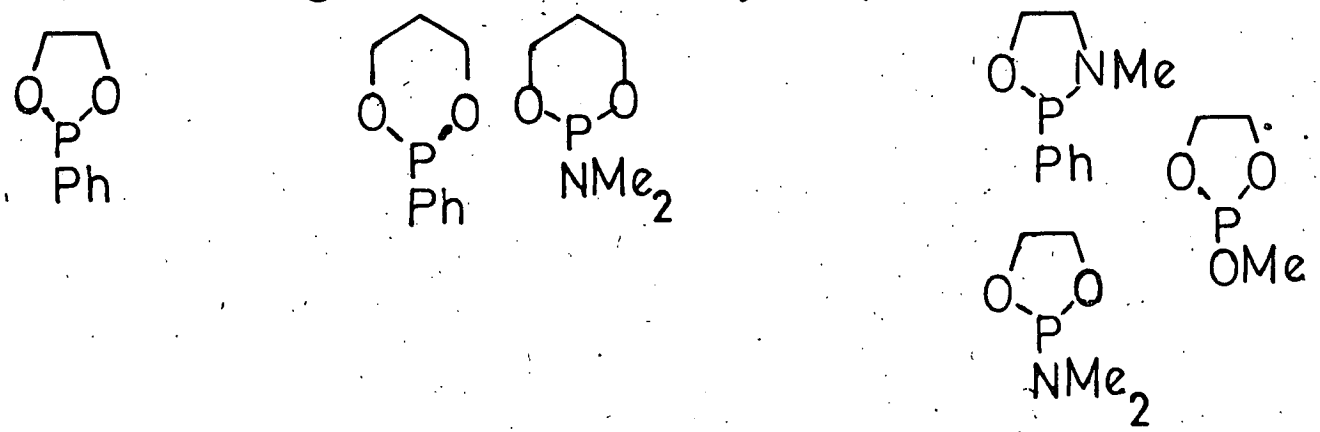
The Complete Series

On consideration of the above discussions a consistent rate series can be put together for all the materials studied, which follows all the previously proposed themes and evidence with regard to trigonal bipyramidal species in such reactions. On one scale there are those materials showing increasing rate with decreasing ring size (with allowances for steric factors) while on the other there are those showing lower than expected rate due to the very stability of the trigonal bipyramidal species involved, viz:

increasing rate due increase in ring strain



increasing rate due stability of penta-coordinate species



That the stability of the penta co-ordinate species plays an important role in reducing the rate of reaction in the second series is shown by the ^{31}P N.m.r. result already mentioned for the N-(4-methyl-2-nitrophenyl)-imino-2-phenyl-1,3,2-dioxaphospholan and that the first series proceeds *via* a rate determining step of formation of such a trigonal bipyramid is indicated as similar ^{31}P N.m.r. studies on N-(4-methoxy-2-nitrophenyl)-imino-1,2,5-triphenylphosphole gave no absorption in the five co-ordinated phosphorus region at any time during the reaction study thereby indicating that the penta co-ordinated species in that particular reaction had no finite lifetime on the ^{31}P N.m.r. time-scale.

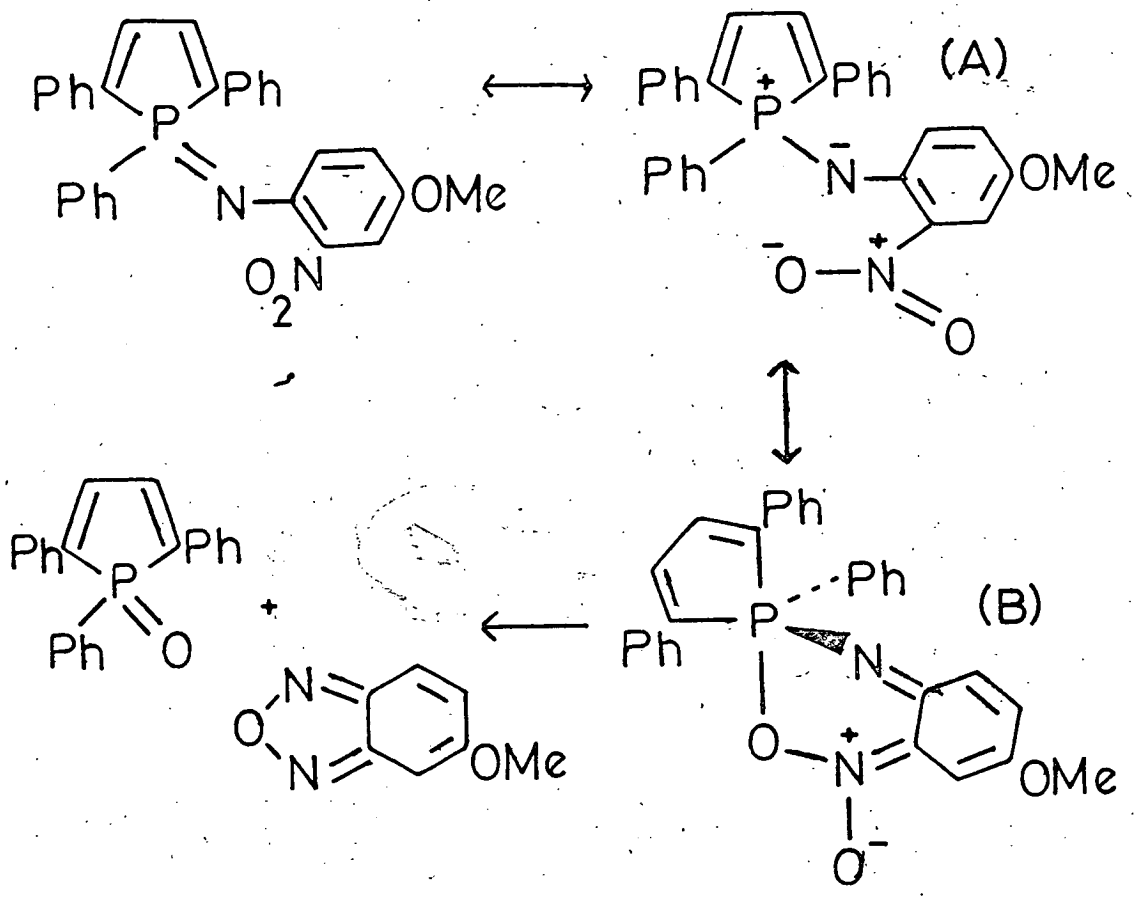
Further evidence for Penta-co-ordinate Species

That the dioxaphospholan ring led to such a result in the ^{31}P N.m.r. is the most conclusive evidence presented to date for the existence in this type of reaction of such penta co-ordinate species. During work on the 1,2,5-triphenyl-phosphole case in the ^{31}P N.m.r. further evidence was obtained.

When N-(4-methoxy-2-nitrophenyl)-imino-1,2,5-triphenyl-phosphole was reacted in bromobenzene a certain rate was observed, viz. $7.58 \times 10^{-3} mn^{-1}$. This was different from that observed for the same molecule in bromobenzene by ^{1}H N.m.r. presumably due to the addition of the deuterium labelled materials used as a "lock". What was more relevant, however, was the dramatic change in rate when *tert*-butylbenzene was used as solvent (Graph 37).

Compared to bromobenzene (dipole moment = 1.5 D), *tert*-butylbenzene is non-polar. In this reaction the postulated

reaction mechanism can be written as follows:

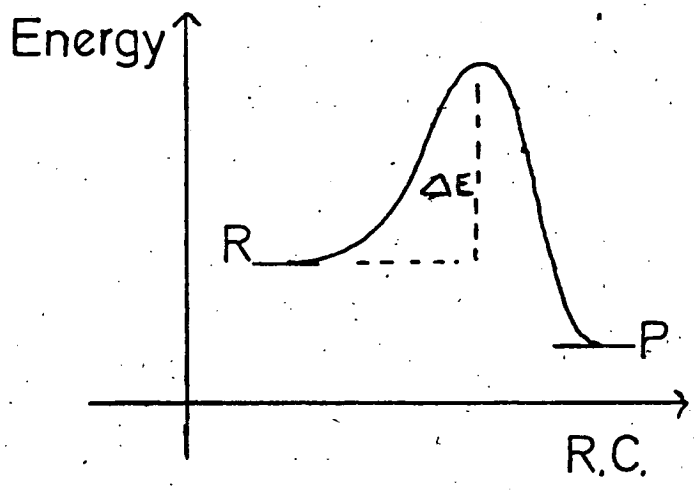


Here then, in proceeding to the penta co-ordinate species (B) from (A), the number of charge separations is reduced from two to one. Hence, any solvent stabilising the less charged species (B) should increase the rate of reaction. That this is so is amply demonstrated by the rapidity of the reaction in tert-butylbenzene, the reaction being complete after only one hour or so and tert-butylbenzene being less polar would be expected to give greater stabilisation of the less polar intermediate or transition state.

The Ring Effect (2)

Further consideration of the energy (E) vs reaction co-ordinate (R.C.) graph may now be useful.

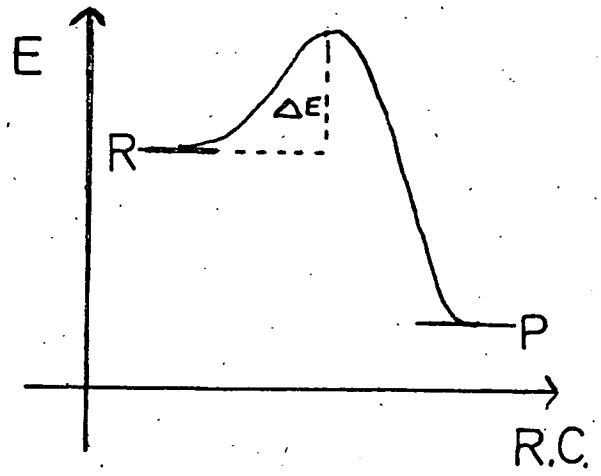
It has been demonstrated that the open-chain species gives no reaction. A graph of the above type would then be expected to look as follows (where R = reactant, P = product).



- where, obviously, the transition energy ΔE is too great to allow the reaction to proceed at 160°C. Indeed further attempts to force this reaction to proceed at elevated temperatures (~250°C) in vacuo failed as well.

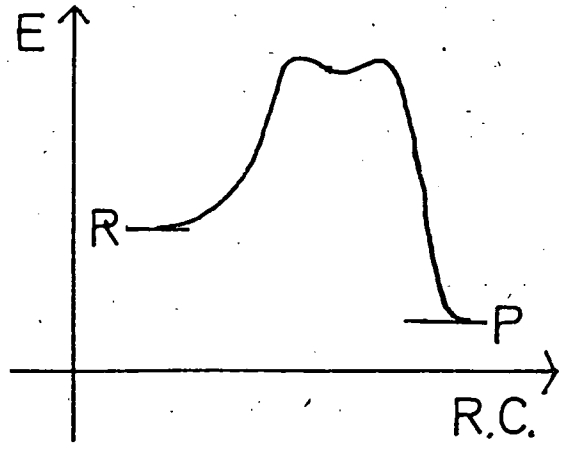
In the case of the 9-phenyl-9-phosphafluorene moeity the steric and electronic considerations discussed above must then give a similar graph.

For each of the varying phosphorus groupings described previously, ΔE must therefore be reduced by the ring strain considerations so that the Energy/Reaction Co-ordinate graph then appears slightly differently -

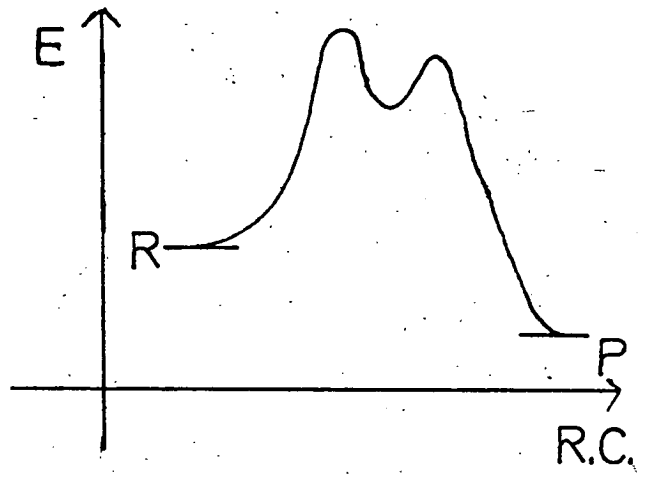


- the relative energy of the reactant and products now being much more widely separated due to the increase in energy of the reactant owing to the internal strains present compared to the open-chain analogue above and the energy gain in forming a phosphorus-oxygen double bond in the product.

In the case of the 2-phenyl-1,3,2-dioxaphospholan (121) case however, the presence of a relatively stable intermediate that, when produced at 160^{o} and then rapidly cooled to room temperature, was still detectable after some 45 to 60 minutes, means an Energy/Reaction Co-ordinate relationship of the following character -

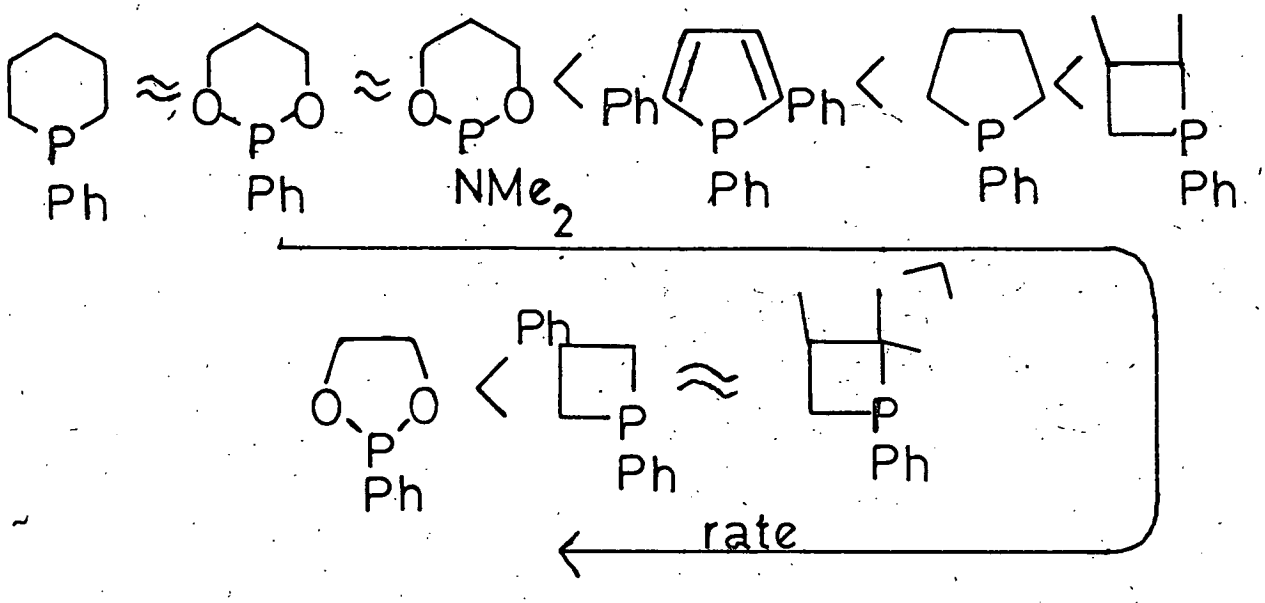


The transition species of the previous types of reaction described in this fashion has now become an intermediate with a life-time dependant on the "depth" of the "trough" in energy terms. In the case in point, that such a species is still detectable after 45-60 minutes at room temperature, while also being detectable in the reaction, with therefore a finite life-time on the ^{31}P N.m.r. time-scale, even at 160° in situ, suggests that the energy trough is relatively deep, i.e.



The question now arises as to whether any of the other species investigated give a similar result.

In fact, the 1,2,5-triphenylphosphole case was investigated in some depth at this point. Even on cooling, the reaction mixture displayed no trace of any such intermediate species. This fact, taken with the phosphetan rate results then suggested that in fact the explanation lay in the relative energy stabilities of the phosphorus moieties and that the series could now be written as a "cyclic" range, viz:



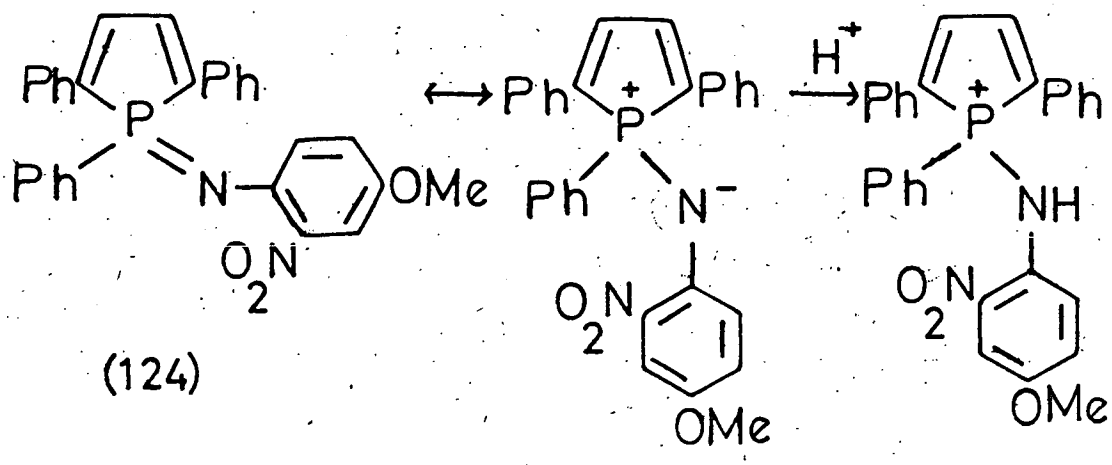
What is now seen is a much more consistent pattern, whereby from six-membered ring to five-membered unsaturated to five-membered saturated there is the expected increase in rate due to increasing ring strain while the four-membered and five-membered dioxaphospholan cases are seen to proceed from this basis in the reverse direction as the transition species becomes more stable. However, in the case of the four-membered ring moieties, there is some doubt whether this result is due to factors such as those discussed on p.145 or more of this type or some combination of both as unfortunately, none of these materials was clean enough on a ^{31}P basis for any detailed examination by this method.

Hydrolysis of N-(4-methoxy-2-nitrophenyl)-imino-1,2,5-triphenylphosphole

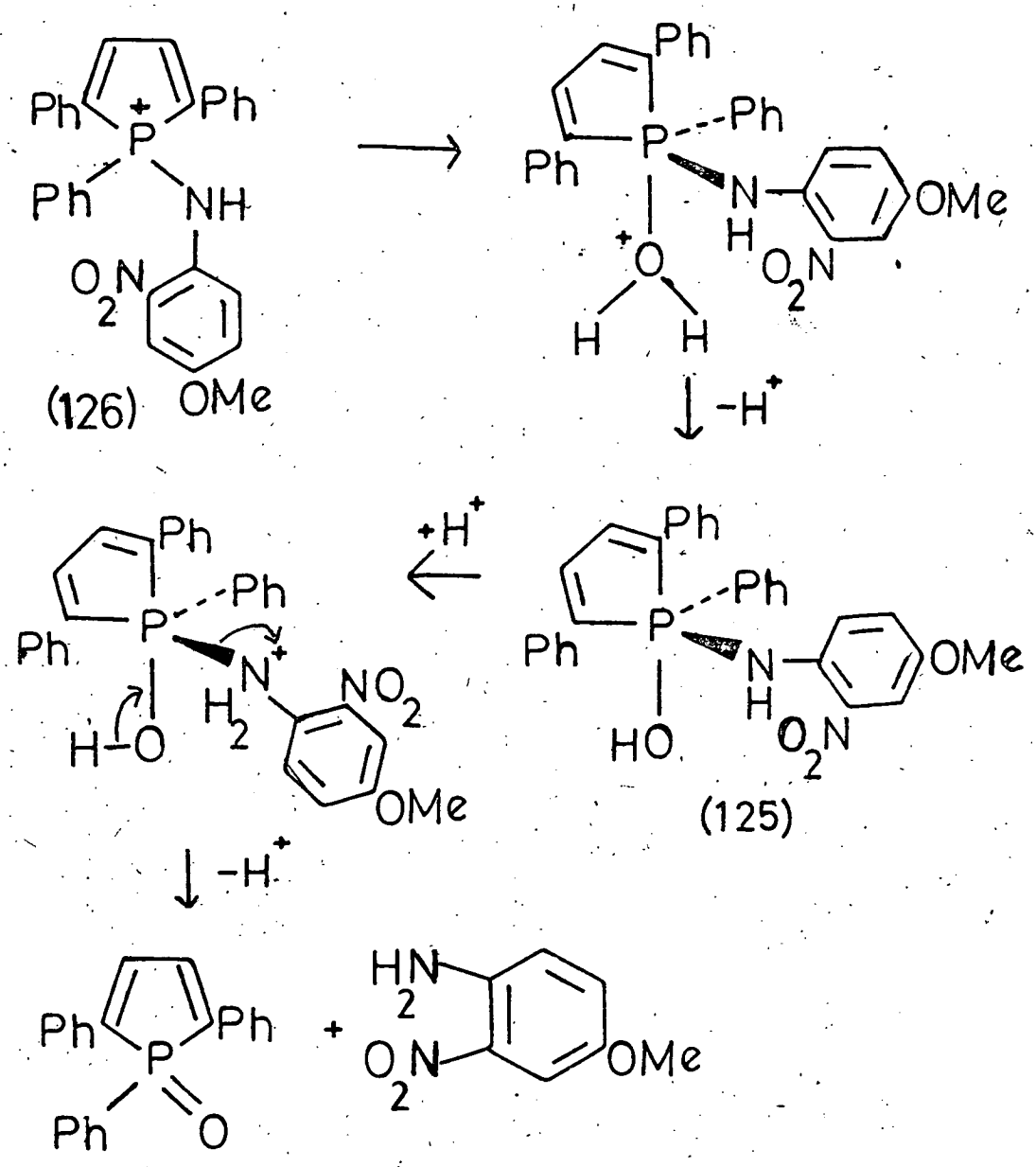
Hydrolysis of the species (124) was found to be extremely rapid at 160° under conditions similar to those used in the other kinetic studies. In fact immersion for 30 seconds appeared to give complete reaction.

An interesting result was noted, however, in the ^{31}P spectrum on hydrolysis at room temperature. This result was the appearance of a broad "peak" in the spectrum between the reactant at +13.0 ppm and the product at +39.0 ppm, the initial reactant disappearing in the acid catalysis conditions used. This, as the reaction progressed, was seen to broaden further and also "move" across the spectrum, starting at an "average" ppm of about 25.9 and finishing at around 33.2 ppm.

Being an acid catalysed reaction, the initial step is taken as being



This protonated species would then be attacked by the water present as follows, leading to the subsequent reaction shown.



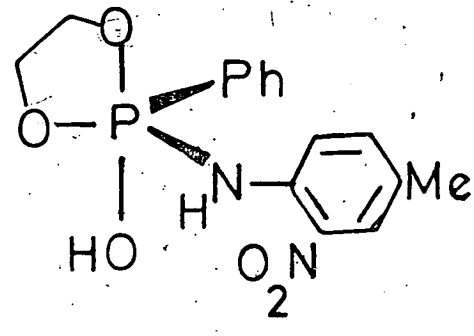
SCHEME 34

Which of these species then is that observed to have a lifetime in the ^{31}P N.m.r.? (125) would appear to be the main candidate as this should be a relatively stable, non charge separated five co-ordinate species. However, this would be expected to appear upfield, at negative ppm, from the four co-ordinate species already noted, as in the case of the intermediate in the thermolysis of N-(4-methyl-2-nitrophenyl)-imino-2-phenyl-1,3,2-dioxaphospholan.

It is suggested, therefore, that what is seen is in fact the charged species (126), stabilised by co-ordination with the water of reaction. As the water of reaction is then used in forming the product, the co-ordination sphere around the charged species would become weaker and the phosphorus ^{31}P shift would be affected, as seen here. This is also supported by the rapid disappearance of the starting material to this species, any arguments in favour of (125) being to some extent discounted as the rate determining step in this reaction should be the attack of water on the positively charged phosphorus atom. That this species in question appears rapidly and then decomposes slowly, therefore, suggests that it is formed in the reaction sequence prior to the attack of water and formation of a P-O bond.

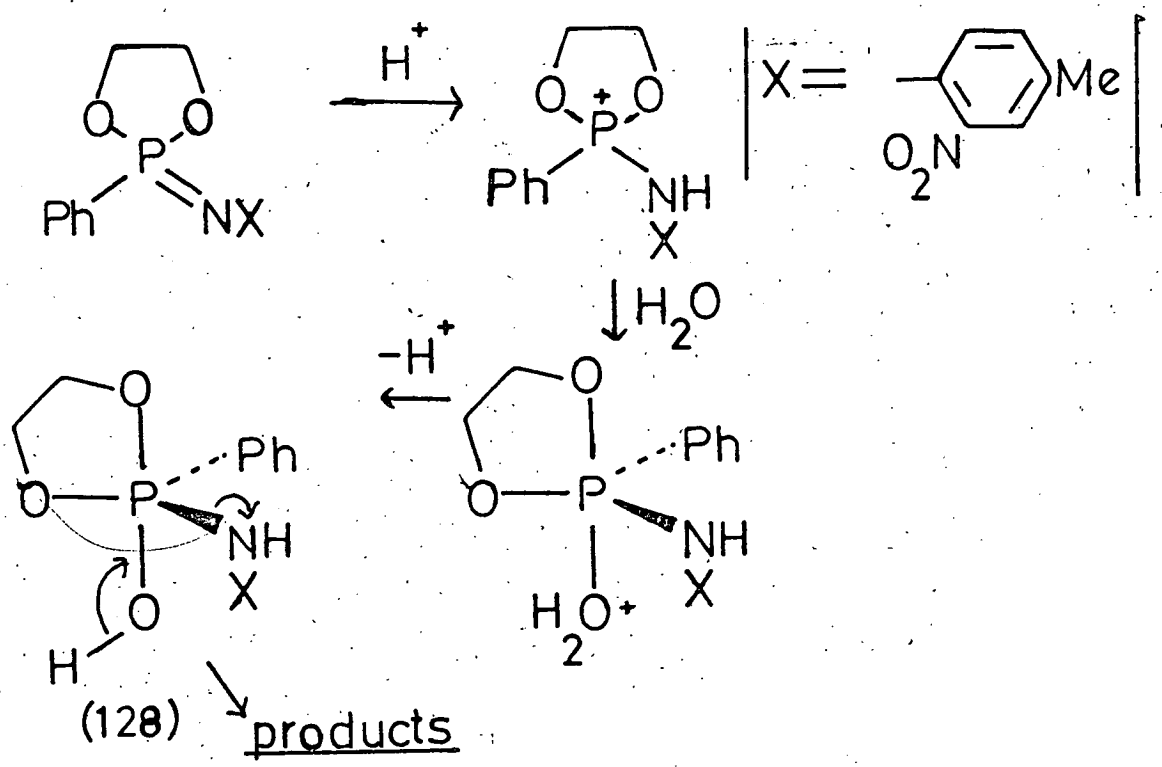
Hydrolysis of N-(4-Methyl-2-nitrophenyl)-imino-2-phenyl-1,3,2-dioxaphospholan

Following the results obtained for hydrolysis above, and in the thermolysis of this compound, great interest centred on whether a species such as (127) could be observed in the hydrolysis of this material.



(127)

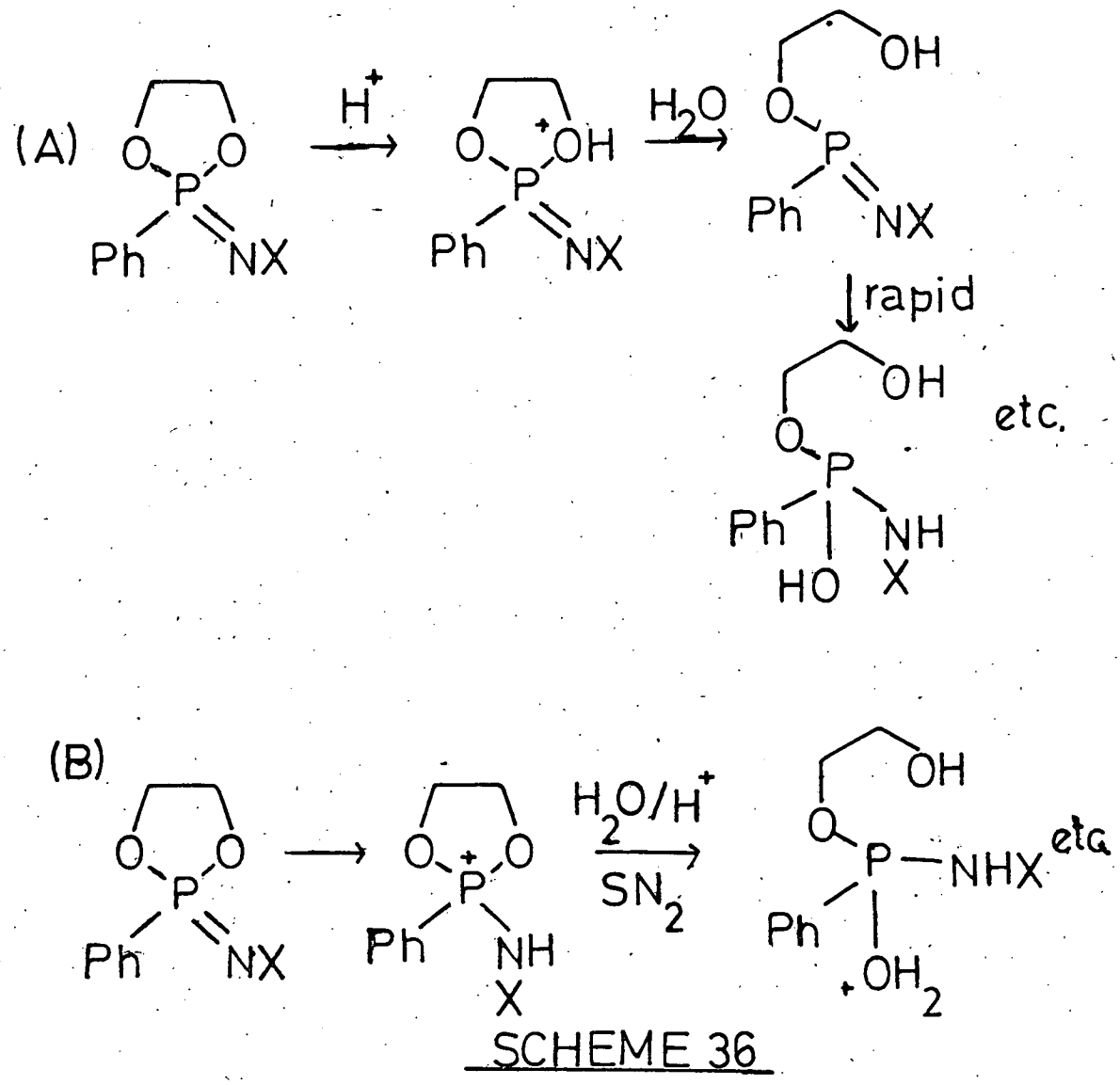
On acid hydrolysis, however, there are so many possible alternative sites for protonation, that the situation is immediately confused, and indeed, several products were observed by ^{31}P N.m.r. The hoped for main reaction was as follows:



SCHEME 35

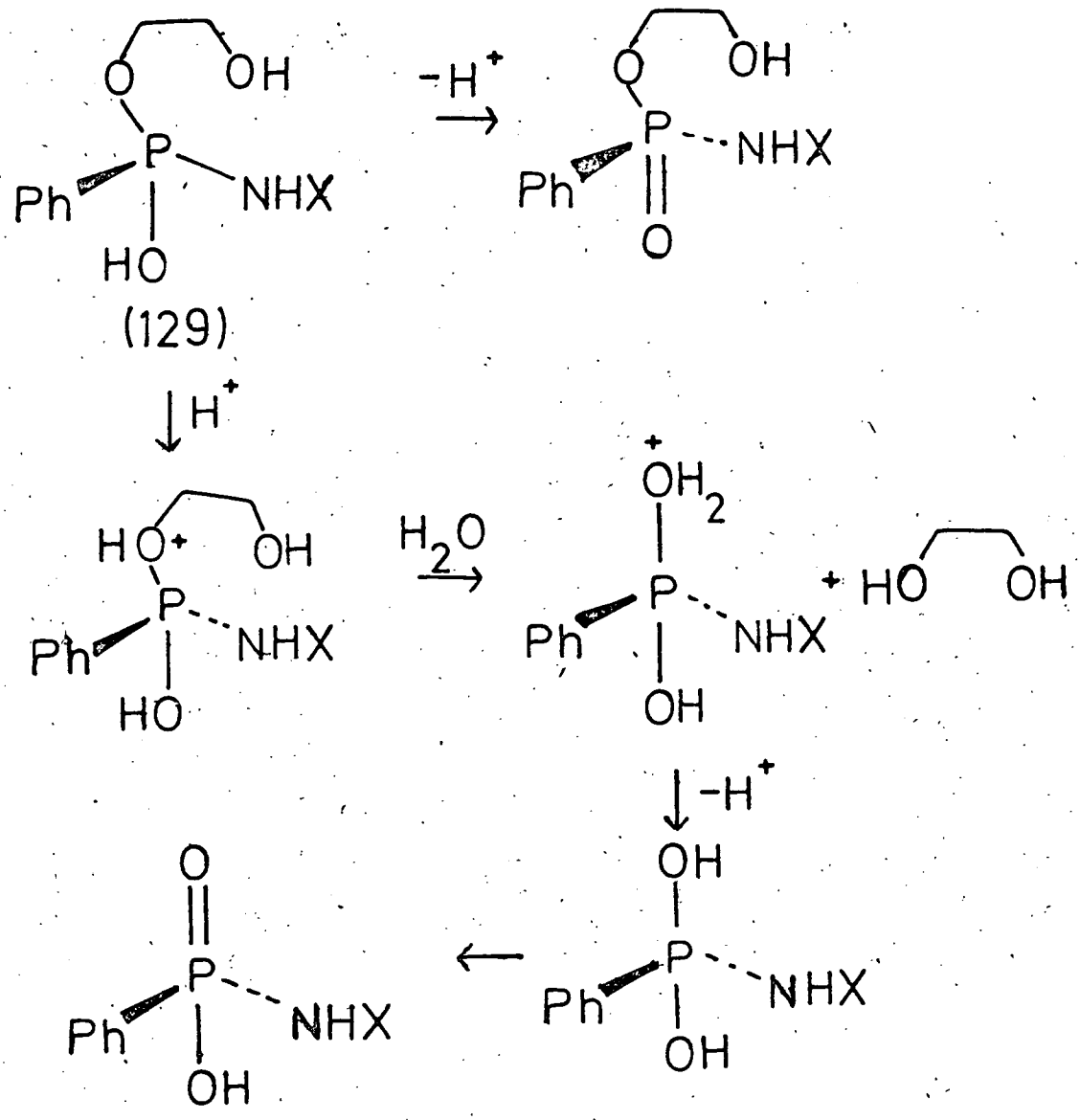
No absorption was noted however, in the expected region for five co-ordinate species, so that, under the prevailing conditions, the five co-ordinate species (128) has too short a life-time to be observed by ^{31}P N.m.r.

The other possible reactions here, obviously parallel those already noted by Ramirez et al.[20] these being:



SCHEME 36

The species (129) can then decompose by various methods also, amongst which are:



SCHEME 37

The Formation of 2,4-disubstituted aniline in the thermolysis reactions

A result not previously noted by Cadogan and Scott in their thermolysis work was the formation of 2-nitro-4-alkyl- or 2-nitro-4-alkoxyaniline in the thermolysis of the phosphorus imines.

This was at first put down to hydrolysis by water in the solvent or n.m.r. tube. After several months study, however, the conclusion was reached that this was in fact a genuine

side-reaction. The evidence for this decision lying in the facts that

(a) despite careful drying of all solvents and reactants and oven-drying of the N.m.r. tubes used, this product could not be eradicated. Indeed, even vacuum sealing of the N.m.r. tubes still resulted in the anilines being observed.

(b) Notwithstanding the actions taken in (a) the quantity of substituted aniline produced remained remarkably constant,

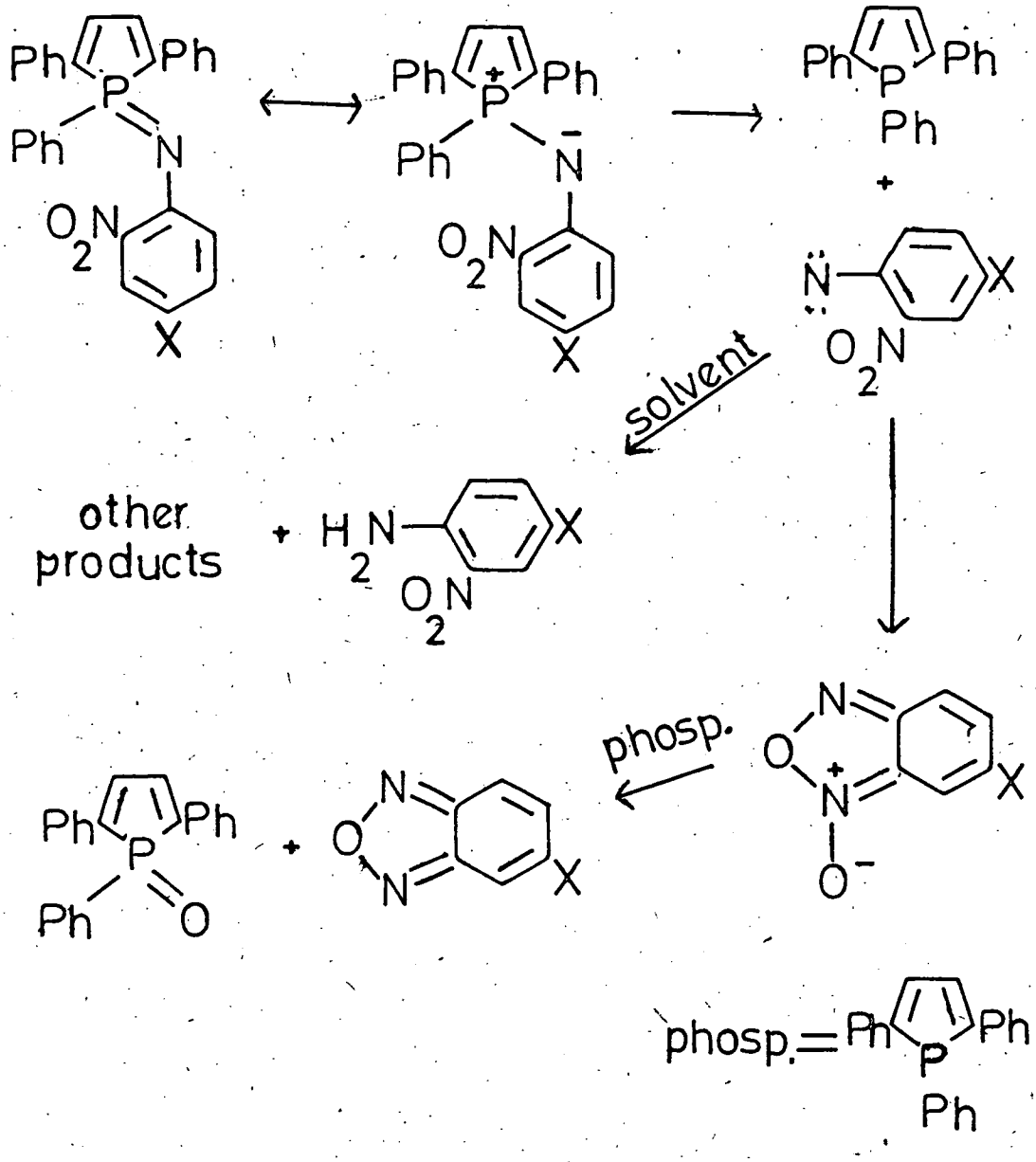
(c) while not conclusive, a study of the same ilk as that for the 5-substituted benzofurazans seemed to indicate that the formation of anilines was a FIRST ORDER reaction. This evidence is not conclusive as the concentration of any water must have been low.

(d) Much more conclusively, a series of thermolyses of the same reactant, under vacuum in a Kügelröhr apparatus, where the solid itself is thermolysed in the absence of solvent, also yielded the same 2,4-disubstituted anilines.

Taking these points in turn, the evidence in (a) for a long time cast doubts on the accuracy of the method involved. It was only when a series of results on the same reactant yielded such close results in terms of percentage yield of the aniline in question that it was believed that this might have been a genuine side-reaction. Why?

The reason for this doubt lay in any conceivable mechanism for generation of an aniline from the reactants in question without the intermediacy of a water molecule. Such a mechanism would almost certainly involve fracture of

the phosphorus nitrogen double bond - this leading to the formation of a nitrenoid species, viz:

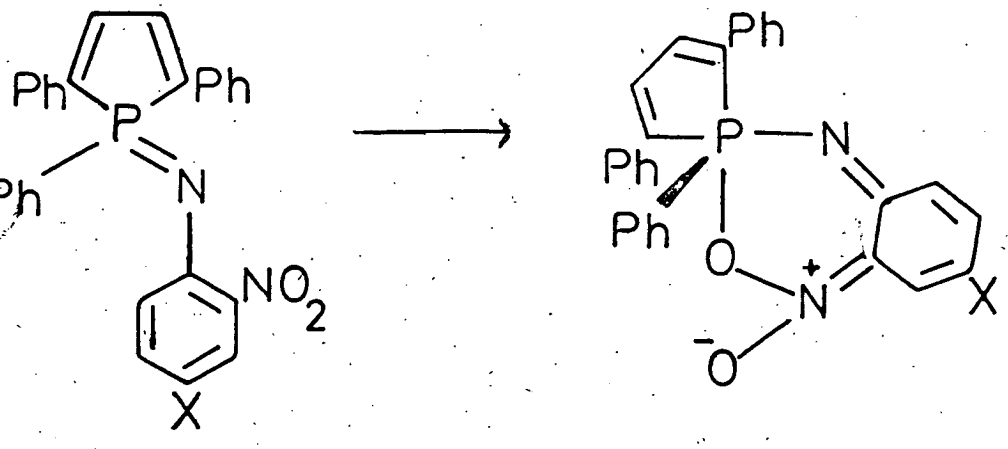


SCHEME 38

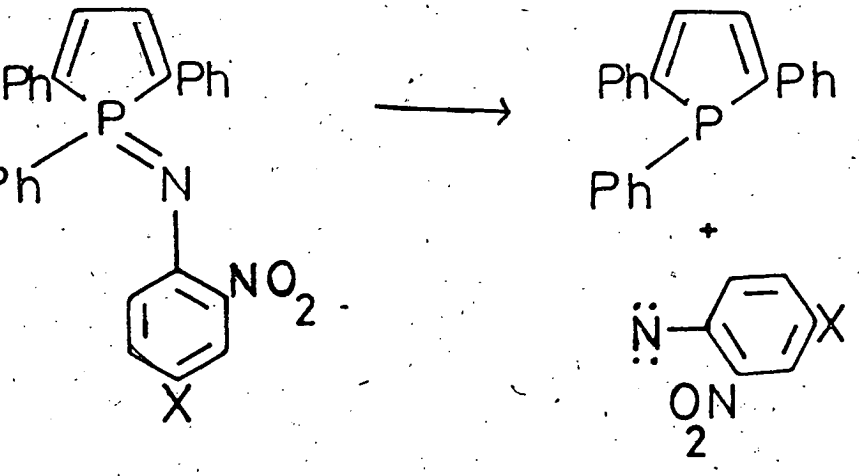
Nitrenoid species are well known to be highly reactive and the hesitation in postulating such a species in the reaction scheme was based on the relative energies of the proposed intermediates or transition species. In nearly all cases, as seen from Table 6, the aniline formation reaction is

seen to be nearly exactly half as fast as that of the benzo furazan formation. Consider the steps for each of these reactions as follows:

A



B



In A, the formation of a P-O bond and relief of ring strain in formation of a five co-ordinate species leads to the suggestion that this should be a likely pathway.
In B, fracture of the P-N double bond, and formation of a highly energetic nitrenoid species would seem to disfavour this pathway, and certainly B would not be expected to be only half as slow as A.

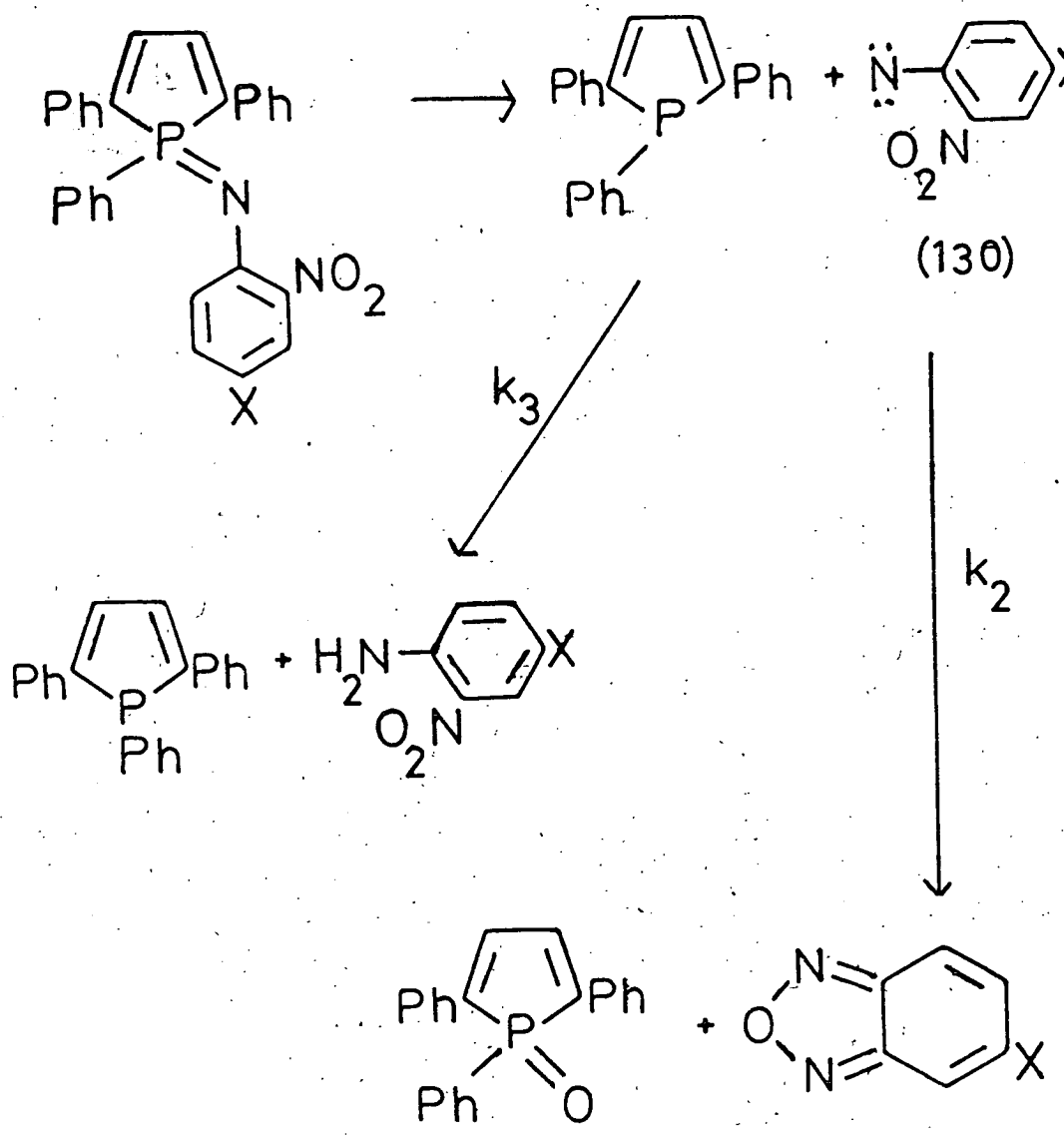
Yet aniline production was noted, in what appeared to be a first order reaction, at such a comparative rate, even when every care had been taken to eradicate water.

Again, however, it must be said that an implied first order reaction is not conclusive, as considering the rate equation for a second order reaction, viz: $k = [\text{Reactant}][H_2O]$, if the concentration of water is low, and approaches zero, then the rate equation is reduced to $k = [\text{Reactant}]$ and gives the impression of a pseudo first order reaction. In this case, at the concentrations in question, this could well have been the case.

The results from the vacuum pyrolysis, however, are much more conclusive, as the glassware was firstly baked in an oven, and the reactants dessicated before pyrolysis. Yet aniline and benzofurazan were observed as products in all three cases attempted.

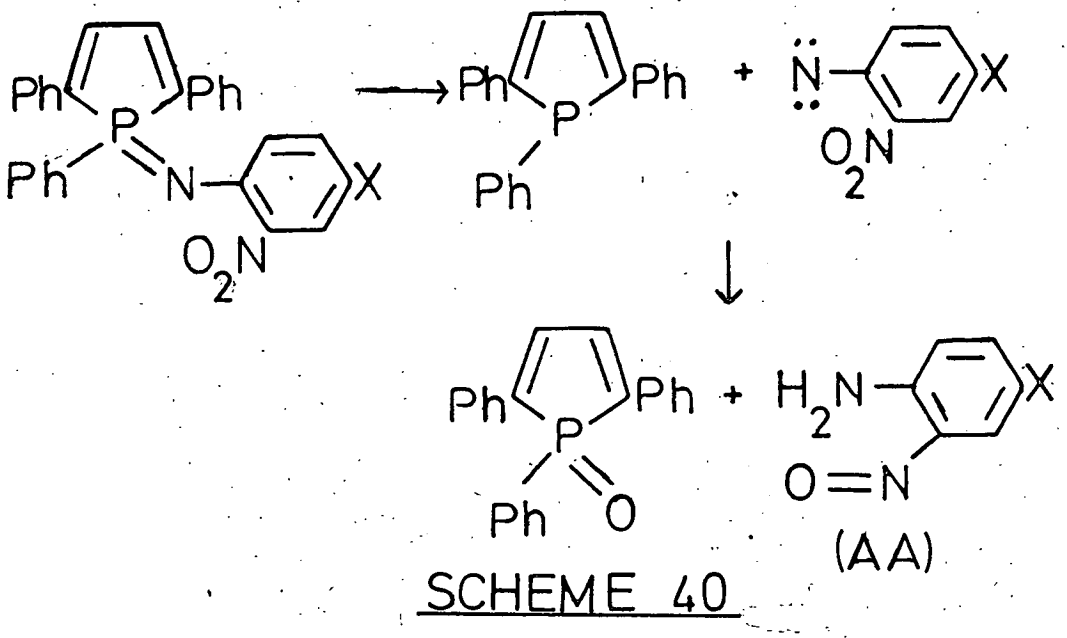
Again, on this occasion the proportions of each were different from that in the thermolysis cases. This immediately suggested a rival mechanism to that proposed initially for the thermolyses.

Consider the following reaction scheme:



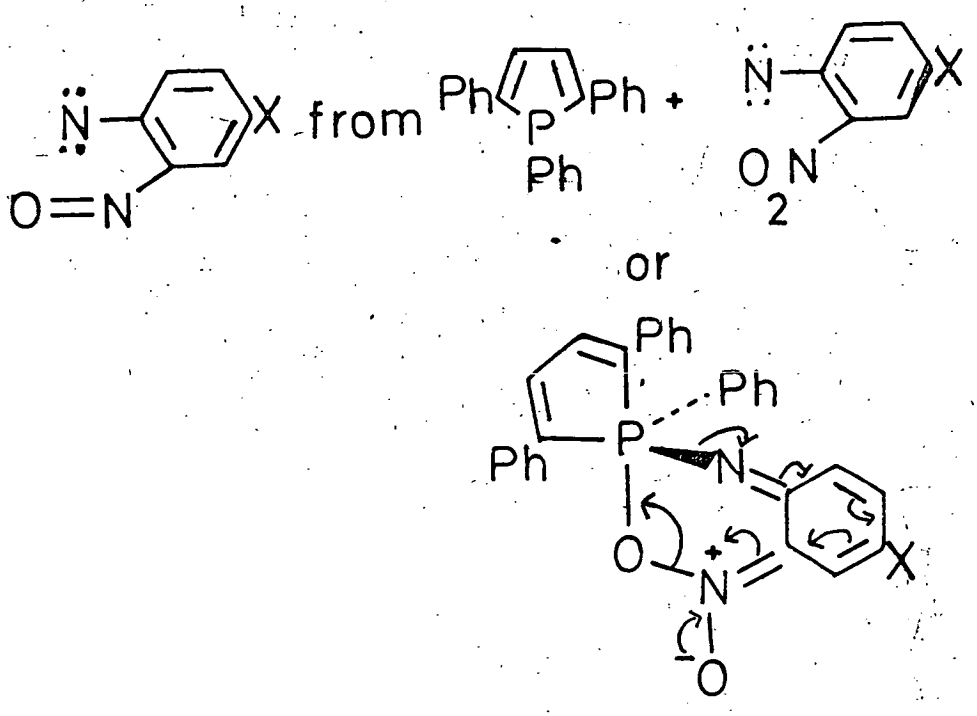
SCHEME 39

In solution, formation of a species such as (130), would lead to several rapid reactions, quite possibly with solvent, to produce the required aniline by hydrogen abstraction. This would tend to suggest the formation then of 1,2,5-triphenylphosphole. No such species was observed however in the ^{31}P N.m.r. spectrum of this reaction, only the 1,2,5-triphenylphosphole oxide. How then does the phosphole, if any, oxidise? A more likely explanation of this observation lies in the scheme



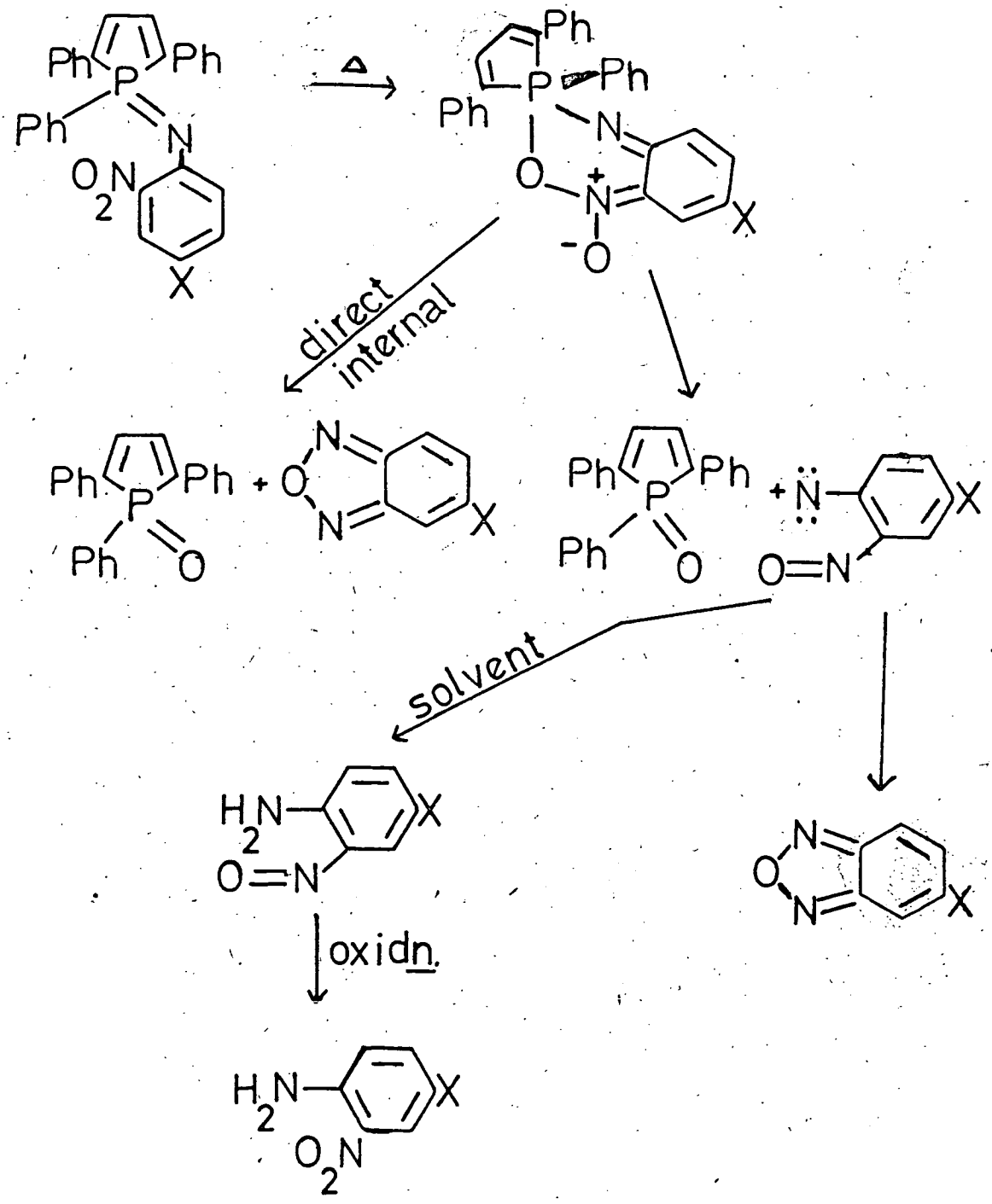
SCHEME 40

On the other hand the species (AA) is highly reactive, and would oxidise rapidly to the required 2-nitroaniline, and an intermediate of the form



could also be seen to produce the 5-substituted benzofurazan directly.

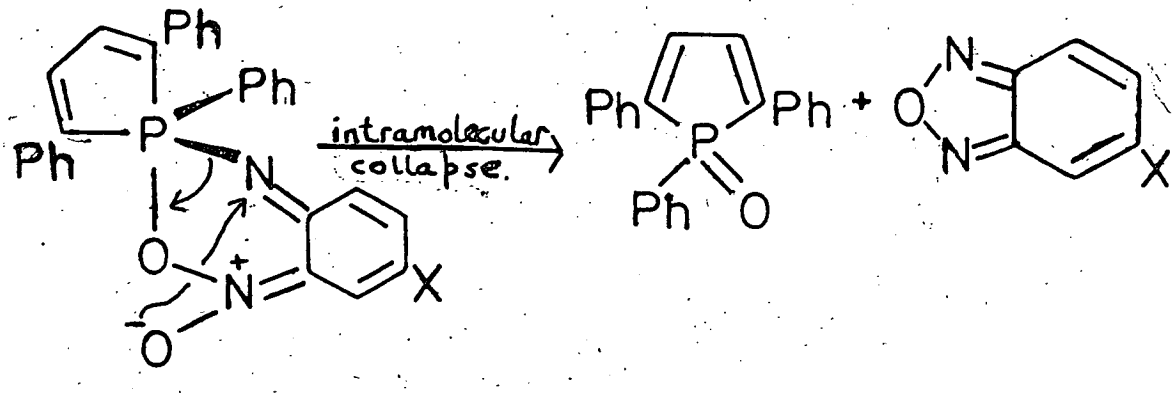
A likely, full, competitive reaction system may then be



SCHEME 41

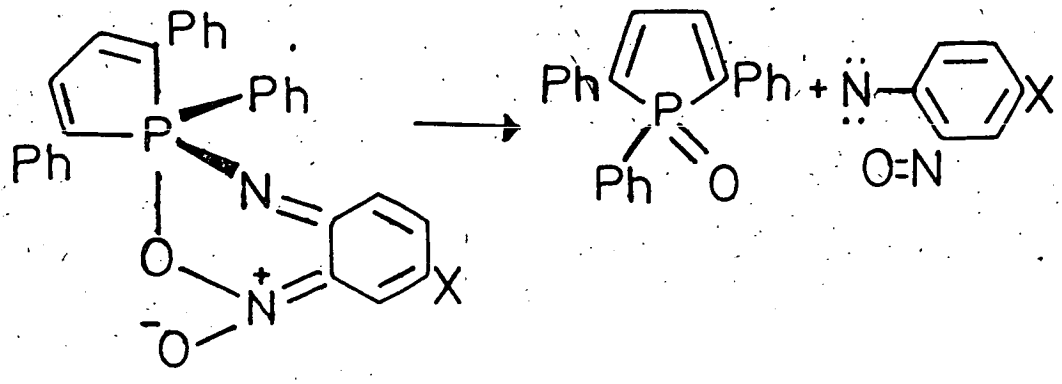
The Mode of Decomposition of Phosphorus Imines

From the preceding discussion, it can now be seen, that a different reaction scheme has been developed to that proposed originally by Cadogan and Scott.[1] In the Scheme above the five co-ordinate intermediate or transition species has two alternative pathways open to it. The first is that proposed by Cadogan and Scott, viz:



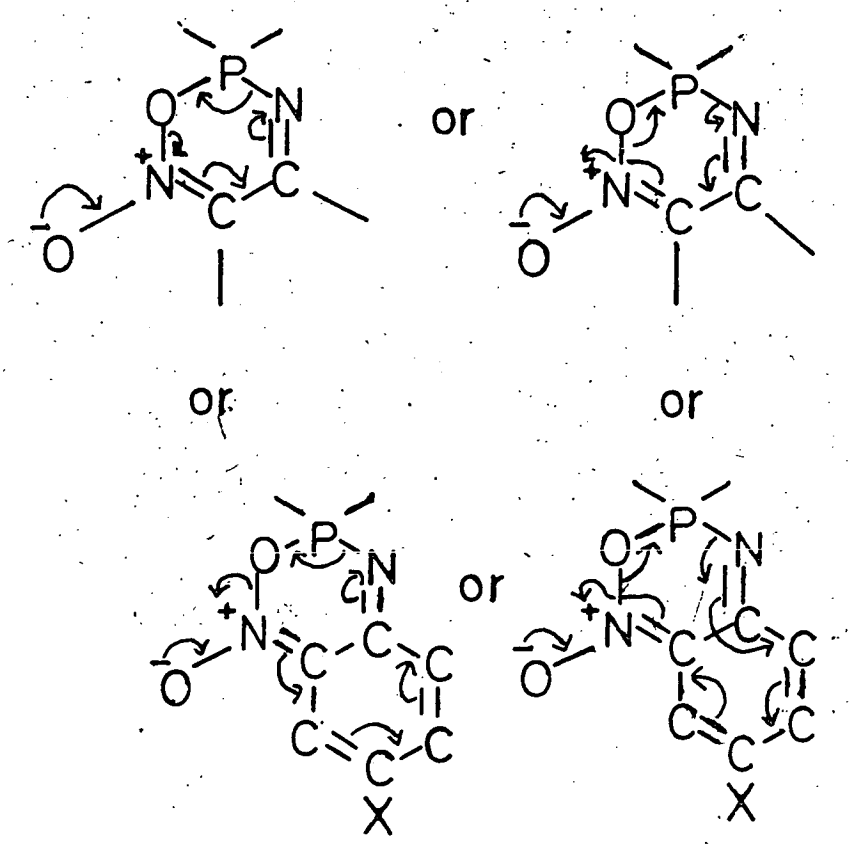
If this were to be the only reaction method, no anilines would be observed.

Secondly, the present proposal, viz:



This second proposal would seem to have certain logical advantages apart from the formation possibilities for anilines. Firstly we still form a five co-ordinate transition species

or intermediate so that all the previous arguments concerning ring strain still hold good. Secondly, the electron flow necessary for decomposition would seem to be much more likely and energetically more favourable than the massive convulsion of the molecule required for decomposition in the original proposal, as the energy required for such a "buckling" of the atomic arrangement in space would seem to cancel all arguments in favour of ring strain being the predominant factor. Also, the electron flow in the second case is <u>via</u> a well-established cyclic six member ring arrangement, with possible use of the benzenoid ring structure, viz:

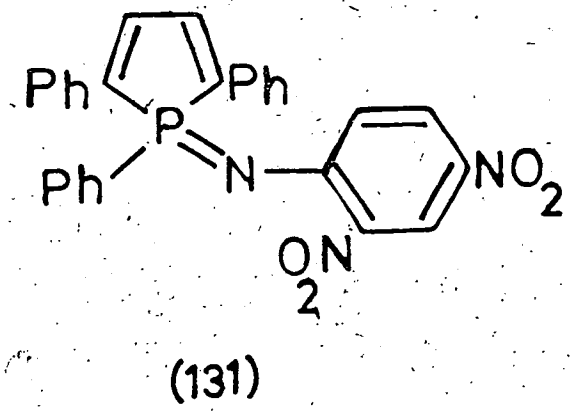


Indeed, that such electron flow should lead to fracture of the phosphorus ring is perfectly feasible, particularly as the spatial arrangement is unlikely to be planar, thereby discounting any stabilising effect via any resonance form due to p, π, or d-orbital overlap.

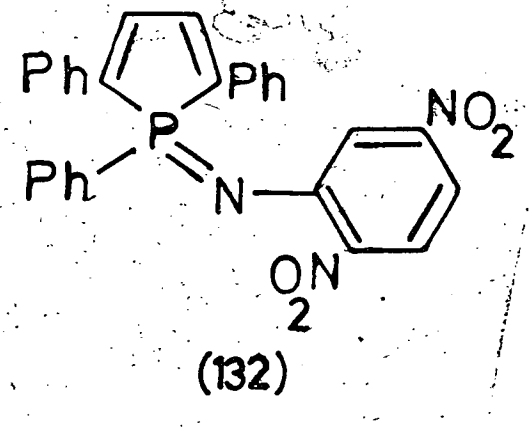
There is also the further, energetically favourable, argument of the re-establishment of aromaticity in the alicyclic ring. Finally, the nitroxide oxygen is a useful "handle" from which to feed the electron cycle.

Effect of Electron Withdrawing Groups on the Benzenoid Ring

More interestingly still, this may also explain why substituents on the benzenoid ring were found by Cadogan and Scott[1,2] to have an effect on the reaction. For example, the phosphorus imine (131), did not undergo decomposition, while (132) did, although slowly.



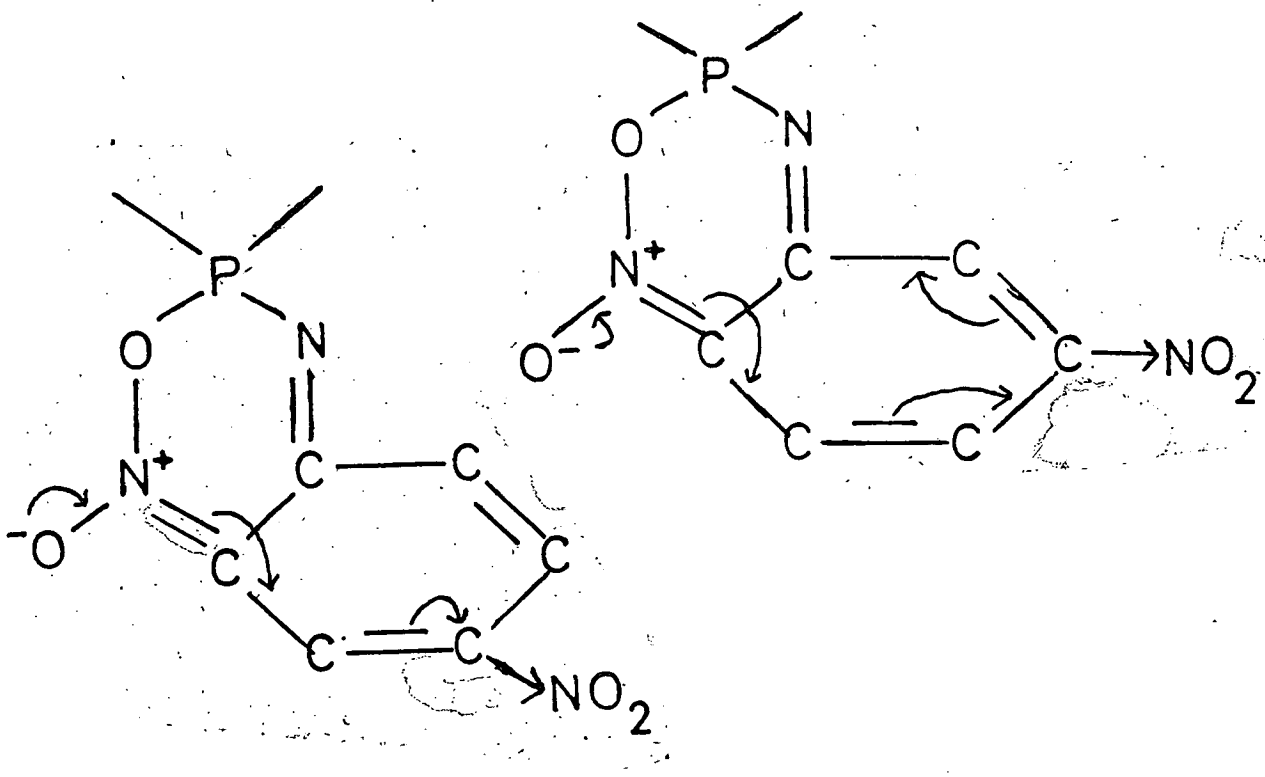
(131)



(132)

Compared to the methyl and methoxyl cases observed in this study, the effect of electron "sinks" such as nitro-groups in the benzenoid ring tends to lend weight to the second proposal, as then in the decomposition step for (131), the nitro-group in the 4-position of the alicyclic ring would

disfavour such electron cycles, while a nitro-group in the 5-position would not have such an extreme effect, viz:



The second proposal then, appears to give logical reasons for all effects so far observed and cannot therefore be discounted.

The Cage Effect

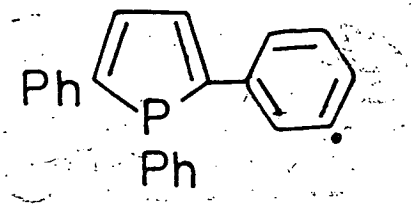
The one argument against a nitrenoid transition species is that there is no real reason why this should form the observed benzofurazans via a nitroso-nitrene rather than rapidly undergo hydrogen abstractions to form anilines. This leads to the formulation of a "cage structure" theory, in that when the five co-ordinate species decomposes, should it form such a nitroso-nitrene there are three pathways open to the electron deficient nitrene, viz:

(a) re-combination with phosphorus,

(b) hydrogen abstraction,

(c) formation of a benzofurazan by attack on the electron rich nitroso group.

Pathway (a) merely means a reversible step in the reaction pathway.

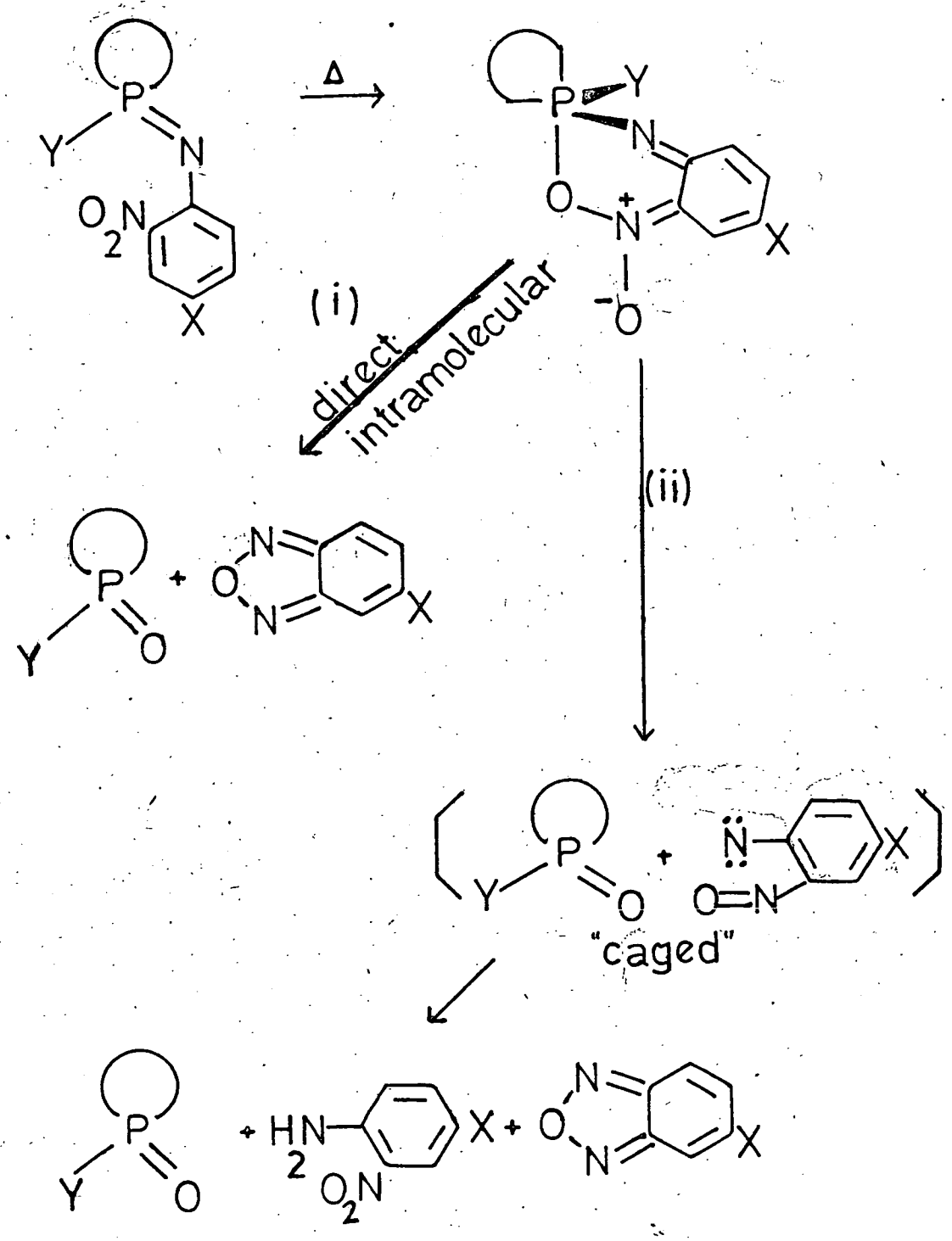
For (b) to occur, the nitrene must have a lifetime sufficiently long enough for it to migrate away from the phosphole oxide and react with solvent, or perhaps via reaction with the phosphole oxide itself, although in solution, this latter is highly unlikely, as formation of species such as  (which would be very reactive) would seem unlikely in the presence of readily available hydrogen abstraction from such as tetramethylsilane, toluene or anisole in the reaction mixtures used in this study.

Should (b) occur readily, then (c) would seem to be unlikely and so it would appear that the migration of any such nitroso-nitrene away from the phosphole oxide moiety formed at the same time must be slow, and this then allows the nitroso-nitrene to react within itself.

As indeed, the most logical reaction for any such species to undergo is rapid re-combination with the phosphorus group, this does in fact seem likely and therefore the phosphorus moiety could well be acting as a "cage" for the nitroso-nitrene, if any such species is formed.

Reaction Scheme for the Intramolecular Decomposition of Phosphorus Imines

From the preceding discussions then, the final reaction scheme proposed for these reactions is as follows:



SCHEME 42

Comparative Rates of the Various Reaction Steps

The rate determining step has been clearly demonstrated as being the formation of the five co-ordinate intermediate or transition species. In comparison therefore steps (i) and (ii) are rapid reactions. Also, within step (ii), three possibilities have been discussed above. Recombination of any nitroso-nitrene with the phosphorus would be expected to be rapid, as would any reaction of such a species. In solution, formation of the anilines, however, by migration and hydrogen abstraction is obviously half as fast as the formation of benzofurazans from such nitrenoid species, judging by the relative proportions of product, provided pathway (i) does not occur.

Thermolysis in Solution vs Pyrolysis in Vacuo

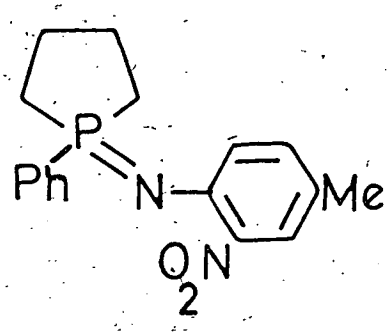
It has already been stated that differing percentage yields were observed for the formation of 5-substituted benzofurazans and 2,4-disubstituted anilines from decomposition in solution and in vacuo.

While it can easily be that the reaction proceeds *via* different mechanisms in solution and in vacuo the most likely answer, in view of the preceding discussions, is that, on formation of a nitrenoid species, in solution, migration of the nitrene can occur to give hydrogen abstraction from solvent. On the other hand, in vacuo, the phosphorus imine is the sole species, so that any hydrogen abstraction reaction must be with itself. In this case then, difficulty in performing such hydrogen abstraction would reduce the yield

of anilinic material and in so doing tend to increase the yield of benzofurazan material.

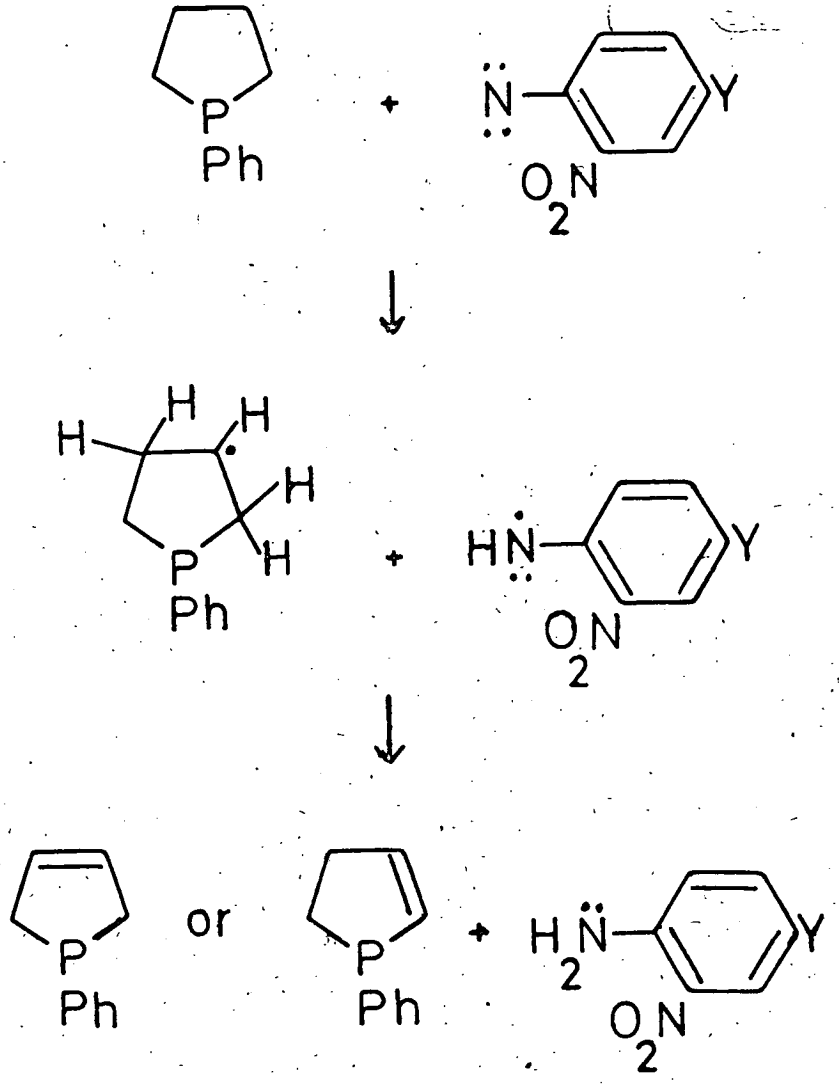
In fact the yield of both materials was reduced significantly in total, but as proposed, the ratio of benzofurazan to aniline material was increased.

A point of interest, and confirmation here, is the in vacuo decomposition of N-(4-methyl-2-nitrophenyl)-imino-1-phenylphospholan (133)



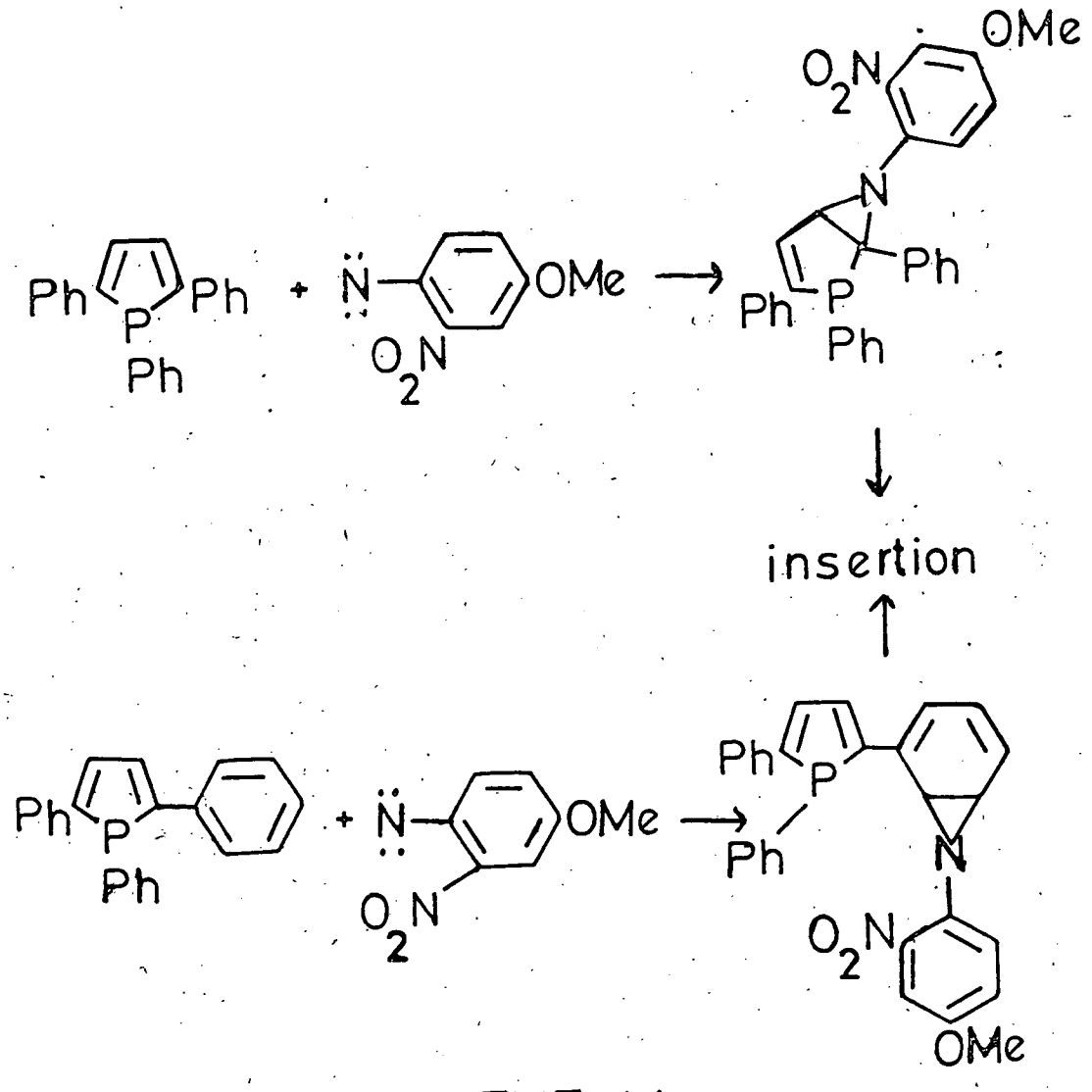
(133)

Here, compared to similar reaction of the corresponding 1,2,5-triphenylphosphole species (124), hydrogen abstraction is relatively easy from the phospholan ring, and in fact, is likely to give relatively stable phospholene species, viz:



SCHEME 43

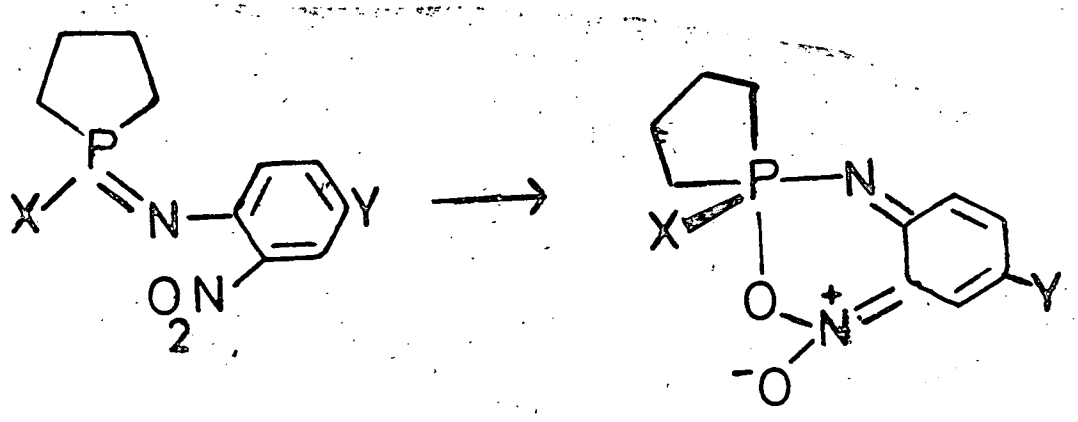
That such reactions may well have occurred, is shown by the large number of "peaks" in the ^{31}P N.m.r. of the red oil which distilled across in this reaction while in both the 1,2,5-triphenylphosphole and 2-phenyl-1,3,2-dioxaphospholan cases, a black tar was produced. Production of such tars is a well known phenomenon in carbene and nitrene chemistry in view of the highly energetic species involved and the multitude of possible reactions which may occur, amongst which in the 1,2,5-triphenylphosphole case could be:



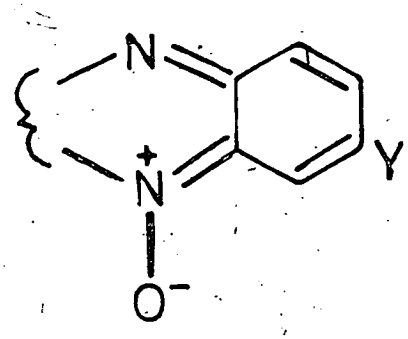
SCHEME 44

Attempts to "Trap-out" the Intermediate or Transition Species Involved

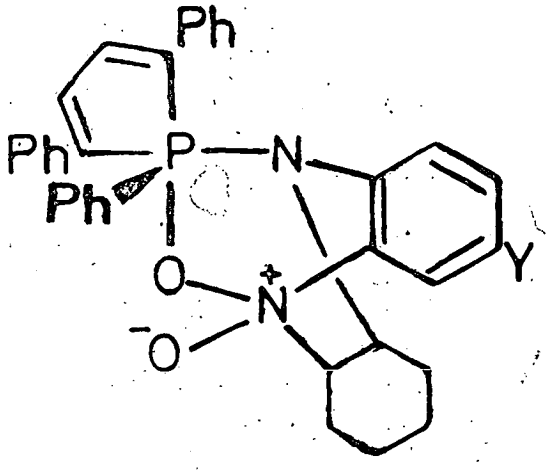
On consideration of the reaction step



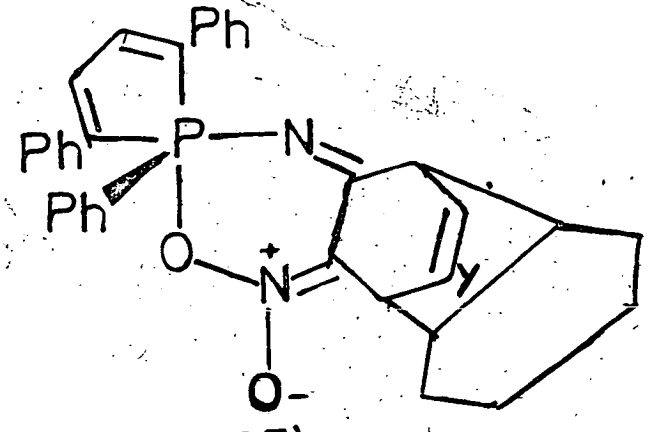
it was felt that, following the preceding arguments in favour of a cyclic electronic movement to give decomposition, that with the arrangement of the "breakaway" atoms in space, viz:



being planar (perforce the conjugated, unsaturated systems involved) that part of this system might well be capable of undergoing a Diels-Alder type reaction with such as cyclohex-1-ene or maleic anhydride. Such a reaction would then lead to species such as (134) and (135):

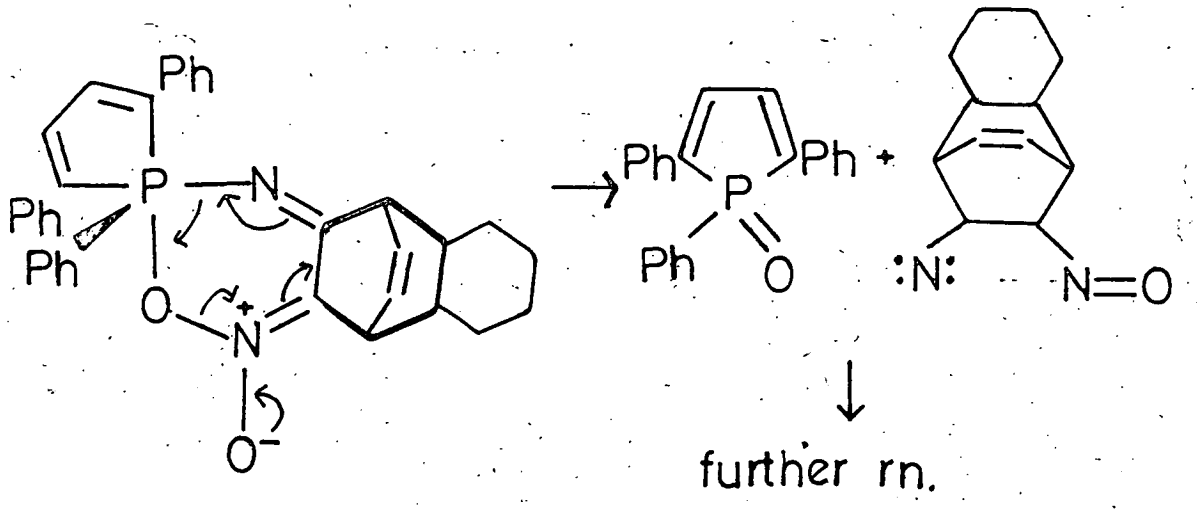


(134)

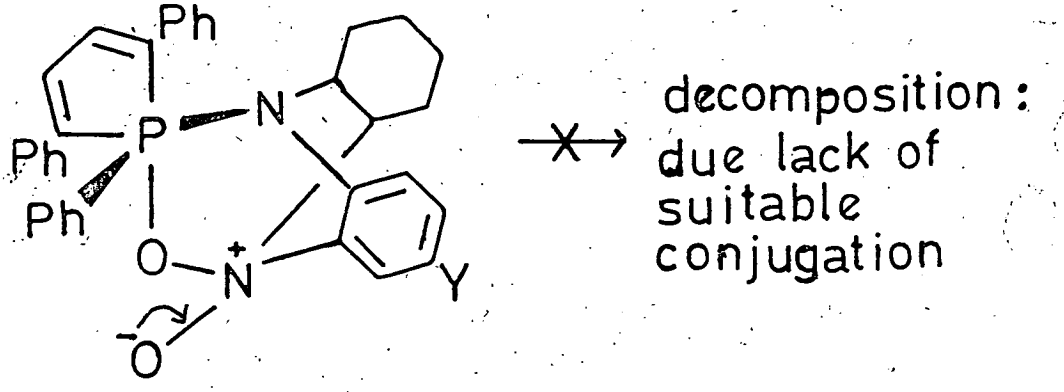


(135)

Whereas (135) would still allow decomposition to occur <u>via</u> electron movement around the cycle shown below



the species (134) would appear to block such movement:



With maleic anhydride however, no points of interest were noted and it was thought more than likely that any reaction could well have been over-ridden by phosphorus reaction with the oxygen moieties of the anhydride.

Attention was therefore focused on reactions with cyclohexene. Reaction of the N-(4-methyl-2-nitrophenyl)-imino-1-phenylphospholan (133) with cyclohexene in bromobenzene at 160°C was shown to give no different products from the usual

decomposition. This could well have been due, in view of the rapidity of the reaction, to the transition species having an insufficient life-time for reaction with the cyclohexene.

The N-(4-methyl-2-nitrophenyl)-imino-2-phenyl-1,3,2-dioxaphospholan gave nil reaction also. In this case, reaction could well be disfavoured in view of the stability of the intermediate involved in this particular decomposition.

Decomposition of N-(4-methoxy-2-nitrophenyl)-imino-1,2,5-triphenylphosphole (124) on the other hand, yielded a red oil, giving a ^{31}P N.m.r. absorption at +7ppm. As the parent species absorbs at +13.0 ppm, 1,2,5-triphenylphosphole at +3.5 ppm, and 1,2,5-triphenylphosphole oxide at +39 ppm, this was without doubt a different phosphoric species. Attempts to identify this material however have failed as no solvent system was found that would selectively crystallise this material and thermolysis and column chromatography led to decomposition.

SUMMARY

Conclusions

(a) Reaction proceeds *via* trigonal bipyramidal transition species or intermediates.

(b) Rate of formation of this species was rate determining in most cases except when stability of this species caused a reduction in rate, the rate of reaction then being governed by the rate of decomposition of this species.

(c) Acid-catalysed hydrolysis proceeds *via* protonation of the imine nitrogen followed by attack of water at phosphorus. The rate determining step being formation of the trigonal bipyramid by attack of water on the protonated imine.

(d) Formation of 2,4-disubstituted anilines as a side reaction, not apparently due to water, suggests but does not prove the presence of a nitrenoid species possible "caged" by phosphorus.

(e) Postulation of a "caged" nitroso-nitrene can indicate rationales for several previously unexplained observations.

(f) No intermediates or transition species have been "trapped" in this reaction due either to too rapid decomposition or inability to identify.

References

1. J.I.G. Cadogan, R. Gee, and R.J. Scott, J.C.S. Chem. Comm., 1972, 1242.
2. J.I.G. Cadogan, R.J. Scott, R. Gee, and I. Gosney, J.C.S. Perkin 1, 1974, 1694.
3. E.L. Eliel, Stereochemistry of Carbon Compounds, McGraw-Hill, 1962, Chp. 9.
4. I. Ugi, P. Gillespie, P. Hoffmann, H. Klusacek, D. Marquarding, S. Pfohl, F. Ramirez, and E.A. Tsolis, Angew. Chem. Int. Ed. Eng., 1971, 10, 687.
5. E.L. Muetterties, W. Mahler, R. Schmutzler, Inorg. Chem., 1963, 2, 613.
6. F.H. Westheimer, Acc. Chem. Res., 1968, 1, 70; and references therein.
7. R.B. Wetzel and G.L. Kenyon, J. Amer. Chem. Soc., 1974, 96, 5199.
8. D.B. Denney, D.Z. Denney, C.D. Hall, K.L. Marsi, J. Amer. Chem. Soc., 1972, 94, 245.
9. N.J. De'Ath, D.Z. Denney, D.B. Denney, and C.D. Hall, Phosphorus, 1973, 205.
10. D.B. Denney, LiShang Shih, J. Amer. Chem. Soc., 1974, 96, 317.
11. D.Z. Denney, D.W. White, D.B. Denney, J. Amer. Chem. Soc., 1971, 93, 2066.
12. N.J. De'Ath and D.B. Denney, J.C.S. Chem. Comm., 1972, 395.
13. E.W. Koos, J.P. Vander Kooi, E.E. Green, and J.K. Stille, J.C.S. Chem. Comm., 1972, 1085.
14. R. Vilceneau, Z. Simon, and A. Chiriac, Chem. Abs., 1973, 79, 145802d.

15. W.E. McEwen, K.F. Kumli, A. Blade-Font, M. Zanger and C.A. Vander Werf, J. Amer. Chem. Soc., 1964, 86, 2378.

16. A. Blade-Font, C.A. Vander Werf and W.E. McEwen, ibid, 1960, 82, 2396.

17. G. Akanes and F.Y. Khalil, Phosphorus, 1972, 2, 105; ibid, 1973, 3, 37, ibid, 1973, 3, 79, ibid, 1973, 3, 109.

18. R. Greenhalgh and R.F. Hudson, Phosphorus, 1972, 2, 1.

19. R.K. Oram and S. Trippett, J.C.S. Perkin 1, 1973, 1300.

20. P. Gillespie, F. Ramirez, I. Ugi, D. Marquarding, Angew. Chem. Int. Ed. Eng., 1973, 12, 91 and ref. therein.

21. K.L. Marsi and R.T. Clark, J. Amer. Chem. Soc., 1970, 92, 3791.

22. K.L. Marsi, J. Amer. Chem. Soc., 1971, 93, 6341.

23. K.L. Marsi, Phosphorus, 1974, 4, 211.

24. J.A. Howard, D.R. Russell, S. Trippett, J.C.S. Chem. Comm., 1973, 856.

25. J.A. Boudreau, C. Brown and R.F. Hudson, J.C.S. Chem. Comm., 1975, 679.

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

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

28. E.L. Muetterties, J. Amer. Chem. Soc., 1969, 91, 1636.

29. G.M. Whitesides and H.L. Mitchell, J. Amer. Chem. Soc., 1969, 91, 5384.

30. I. Ugi, D. Marquarding, H. Klusacek, G. Gokel and P. Gillespie, Angew. Chem. Int. Ed. Eng., 1970, 9, 703.

31. R. Hoffmann, J.M. Howell and E.L. Muetterties, J. Amer. Chem. Soc., 1972, 94, 3047.

32. E.E-Tsolis, F. Ramirez, J.F. Pilot and C.P. Smith, Phosphorus, 1974, 4, 109.

33. G. Akanes and A.I. Eide, Phosphorus, 1974, 4, 209.

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

35. G.W. Fenton, L. Hey and C.K. Ingold, J. Chem. Soc., 1933, 989.

36. M. Zanger, C.A. Vander Werf and W.E. McEwen, J. Amer. Chem. Soc., 1959, 81, 3806; A. Blade-Font, C.A. Vander Werf and W.E. McEwen, ibid, 1960, 82, 2646; C.B. Parisek, C.A. Vander Werf and W.E. McEwen, ibid, 1960, 82, 5503; A. Blade-Font, C.A. Vander Werf and W.E. McEwen, ibid, 1962, 84, 677.

37. R. Schmutzler, Angew. Chem. Int. Ed. Eng., 1965, 4, 496.

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

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

40. C. Brown, J.A. Boudreau, B.H. Hewitson and R.F. Hudson, J.C.S. Chem. Comm., 1975, 504.

41. R. Schmutzler, Angew. Chem. Int. Ed. Eng., 1964, 3, 753.

42. D.B. Denney, D.Z. Denney and Y.F. Hou, Phosphorus, 1974, 4, 213.

43. K.E. DeBruin, A.G. Padilla, M-T Campbell, J. Amer. Chem. Soc., 1973, 95, 4681.

44. J. Emsley, T.B. Middleton and J.K. Williams, J.C.S. Dalton, 1974, 633.

45. J. Hinze, M.A. Whitehead and H.H. Jaffe, J. Amer. Chem. Soc., 1963, 85, 148.

46. D. Gorenstein and F.H. Westheimer, J. Amer. Chem. Soc., 1970, 92, 634; D. Gorenstein, ibid, 1970, 92, 644.

47. E.A. Dennis and F.H. Westheimer, J. Amer. Chem. Soc., 1966, 88, 3431 and 3432.

48. M.J.P. Harger, J.C.S. Chem. Comm., 1971, 442.

49. J.R. Corfield, M.J.P. Harger, R.K. Oram, D.J.H. Smith and S. Trippett, J.C.S. Chem. Comm., 1970, 1350.

50. W. Hawes and S. Trippett, J. Chem. Soc. (C), 1969, 1465.

51. B.R. Ezzell, J. Org. Chem., 1970, 2426.

52. B.R. Ezzell and L.D. Freedman, J. Org. Chem., 1969, 1777.

53. B.R. Ezzell and L.D. Freedman, J. Org. Chem., 1970, 241.

54. K.L. Marsi and J.E. Oberlander, J. Amer. Chem. Soc., 1973, 200.

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

56. F. Matthey, Tetrahedron, 1972, 28, 4181; ibid, 1973, 29, 707.

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

58. N.E. Waite and J.C. Tebby, J. Chem. Soc. (C), 1970, 386.

59. E.H. Braye, W. Hübel and I. Caplier, J. Amer. Chem. Soc., 1961, 83, 4406.

60. I.G.M. Campbell, R.C. Cookson, M.H. Hocking and A.N. Hughes, J. Chem. Soc. (C), 1965, 2184.

61. U. Schmidt, I. Brie, C. Osterroht, R. Schröer and H-F. Gruntzmacher, Chem. Ber., 1968, 101, 1381.

62. J.I.G. Cadogan, R.J. Scott and N.H. Wilson, J.C.S. Chem. Comm., 1974, 902.

63. H.J. Beatmann and G. Hofmann, Annalen, 1968, 716, 98.

64. J.I.G. Cadogan, J. Chem. Soc., 1961, 3067.

65. R. Greenhalgh and R.F. Hudson, J.C.S. Chem. Comm., 1969, 325.

66. R.F. Hudson and R. Woodcock, J.C.S. Chem. Comm., 1971, 1050.

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

68. H.G. Khorana, G.M. Tener, R.S. Wright and J.G. Moffatt, J. Amer. Chem. Soc., 1957, 79, 430.

69. G. Akanes and K. Bergesen, Acta. Chem. Scand., 1965, 19, 931.

70. J.R. Cox, Jr., and O.B. Ramsay, Chem. Rev., 1964, 332.

71. S.E. Cremer, B.C. Trivedi and F.L. Weitl, J. Org. Chem., 1971, 36, 3226.

72. R.F. Hudson and C. Brown, Acc. Chem. Res., 1972, 5, 204 and ref. therein.

73. D.G. Gorenstein, D. Kar, B.A. Luxon and R.K. Momii, J. Amer. Chem. Soc., 1976, 98, 1668.

74. R.R. Holmes, J. Amer. Chem. Soc., 1974, 96, 4143.

75. A . Schnell and J.C. Tebby, J.C.S. Chem. Comm., 1975, 134.

76. K.E. DeBruin and D.M. Johnson, J. Amer. Chem. Soc., 1973, 95, 4675.

77. R.D. Bertrand, H.J. Berwin, G.K. McEwen, J.G. Verkade, Phosphorus, 1974, 4, 81.

78. G. Akanes and D. Akanes, Acta. Chem. Scand., 1964, 18, 1623.

79. W.C. Archie and F.H. Westheimer, J. Amer. Chem. Soc., 1973, 5955.

80. F. Ramirez, V.A.V. Prasad, and J.F. Maracek, J. Amer. Chem. Soc., 96, 7269.

81. A. Munoz, G. Gence, M. Koenig and R. Wolf, Bull. Soc. Chim. Fr., 1975, 1433.

82. F.H. Westheimer, and C.L. Lerman, J. Amer. Chem. Soc., 1976, 98, 179.

83. K. Bergesen, Acta. Chem. Scnad., 1967, 1587.

84. W. Hawes and S. Tripett, J.C.S. Chem. Comm., 1968, 577.

85. J.R. Corfield, M.J.P. Harger, J.R. Shutt and S. Trippett, J. Chem. Soc. (C), 1970, 1855.

86. S.E. Cremer, R.J. Chorvat, Tetrahedron Letters, 1968, 413.

87. P. Haake and P.S. Ossip, Tetrahedron Letters, 1970, 4841.

88. P. Haake, R.D. Cook, W. Schwarz and D.R. McCoy, Tetrahedron Letters, 1968, 5251.

89. P. Haake and T. Koizumi, Tetrahedron Letters, 1970, 4849.

90. P. Haake, R.D. Cook, T. Koizumi, P.S. Ossip, W. Schwarz and D.A. Tyssee, J. Amer. Chem. Soc., 1970, 92, 3828.

91. P. Haake and P.S. Ossip, J. Amer. Chem. Soc., 1971, 93, 6924.

92. R.F. Hudson and L. Keay, J. Chem. Soc., 1960, 1859.

93. M.P. Harger, J.C.S. Perkin 1, 1975, 514.

94. J.I.G. Cadogan and D.T. Eastlick, J.C.S. Chem. Comm., 1973, 238.

95. G. Zon, K.E. DeBruin, K. Naumann and K. Mislow, J. Amer. Chem. Soc., 1969, 91, 7023.

96. S.E. Cremer, J.C.S. Chem. Comm., 1970, 616.

97. J.R. Corfield, R.K. Oram, D.J.H. Smith and S. Tripett, J.C.S. Perkin I, 1972, 713.

98. S.E. Cremer and B.C. Trivedi, J. Amer. Chem. Soc., 1969, 7200.

99. D.J.H. Smith and S. Tripett, J.C.S. Chem. Comm., 1969, 855.

100. D.J.H. Smith, Chem. Soc. Spec. Per. Rep. Organophosphorus Chemistry, 1972, 3, 20.

101. S.E. Cremer, F.L. Weitl, F.R. Farr, P.W. Kremer, G.A. Gray and H. Hwang, J. Org. Chem., 1973, 38, 3199.

102. H.A. El-Seoud Aly, D.J.H. Smith and S. Trippett, Phosphorus, 1974, 4, 205.

103. K. Mislow, Acc. Chem. Res., 1970, 3, 321.

104. W.S. Wadsworth, J. Org. Chem., 1974, 39, 984.

105. K.E. De Bruin and D.M. Johnson, J. Amer. Chem. Soc., 1973, 95, 7921.

106. I. Granoth, Y. Segall and H. Leader, J.C.S. Chem. Comm., 1976, 74.

107. T.D. Inch, G.J. Lewis, R.G. Wilkinson and P. Watts, J.C.S. Chem. Comm., 1975, 500.

108. J.I.G. Cadogan, D.T. Eastlick, J.A. Challis and A. Cooper, J.C.S. Perkin II, 1973, 1798.

109. R.F. Hudson and M. Green, Angew. Chem. Int. Ed. Eng., 1963, 2, 11.

110. V. Mark, J. Amer. Chem. Soc., 1963, 85, 1884.

111. R.F. Hudson, R.J.G. Searle and F.H. Devitt, J. Chem. Soc.(B), 1966, 789.

112. R.F. Hudson and R.J.G. Searle, ibid, 1968, 1349.

113. D.W. Allen, B.G. Hatby and K. Polasik, J.C.S. Perkin I, 1975, 619.

114. S. Fliszar, R.F. Hudson and G. Salvadori, Helv. Chim. Acta, 1963, 1580.

115. G. Wittig and U. Schöllkopf, Chem. Ber., 1954, 87, 1318.

116. R.F. Hudson and P.A. Chopard, Helv. Chim. Acta, 1963, 2178.

117. S. Fliszar, R.F. Hudson and G. Salvadori, Helv. Chim. Acta, 1964, 159.

118. P.A. Chopard, R.F. Hudson and R.J.G. Searle, Tetrahedron Letters, 1965, 2357.

119. G. Märkl, Angew. Chem. Int. Ed. Eng., 1962, 1, 511.

120. G. Märkl, Angew. Chem. Int. Ed. Eng., 1965, 1023.

121. G. Märkl, Angew. Chem. Int. Ed. Eng., 1967, 87.

122. H. Kise, J.C.S. Chem. Comm., 1976, 299.

123. L.I. Chang, D.Z. Denney, D.B. Denney and Y.F. Hsu, Phosphorus, 1974, 4, 265.

124. R.L. Dannley, R.L. Waller, R.V.Hoffman and R.F. Hudson, J.C.S. Chem. Comm., 1971, 1362.

125. R.L. Dannley and K.R. Kabre, J. Amer. Chem. Soc., 1965, 87, 4805.

126. P.A. Chopard, V.M. Clark, R.F. Hudson and A.J. Kirby, Tetrahedron, 1965, 21, 1961.

127. A. Schmidpater and J. Luber, Phosphorus, 1975, 5, 55.

128. E. Evangelidou-Tsolis, F. Ramirez, J.F. Pilot and C.P. Smith, Phosphorus, 1974, 4, 109.

129. J.I.G. Cadogan, D.S.B. Grace, P.K.K. Lim and B.S. Tait, J.C.S. Chem. Comm., 1972, 520.

130. J.I.G. Cadogan, R.O. Gould and N.J. Tweddle, J.C.S. Chem. Comm., 1975, 773.

131. R.F. Hudson and A. Mancuso, J.C.S. Chem. Comm., 1969, 522.

132. R.F. Hudson and R.J.G. Searle, J.C.S. Chem. Comm., 1967, 1249.

133. R.F. Hudson and A. Mancuso, Tetrahedron Letters, 1971, 3821.

134. R. Greenhalgh, J.E. Newberry, R. Woodcock and R.F. Hudson, J.C.S. Chem. Comm., 1969, 22.

135. C.R. Hall and D.J.H. Smith, Tetrahedron Letters, 1974, 1693.

136. G. Aksnes and P. Frøyen, Acta Chem. Scand., 1969, 23, 2697.

137. G. Aksnes and P. Frøyen, Acta Chem. Scand., 1970, 24, 809.

138. D.G. Smith and D.J.H. Smith, J.C.S. Chem. Comm., 1975, 459.

139. K. Issleib and E. Priebe, Chem. Ber., 1959, 92, 3183.

140. R.J. Scott, Ph.D. Thesis, University of Edinburgh, 1973.

141. B.J. Walker, Organophosphorus Chemistry, Penguin, Middx., 1972, 162.

Experimental Section References

142. A.I. Vogel, 'A Textbook of Practical Organic Chemistry', Longmans, 1956.

143. A.O. Fitton, R.K. Smalley, 'Practical Heterocyclic Chemistry', Academic Press, 1968.

144. Beilstein's Handbuch der Organischen Chemie, Springer-Verlag, 1956.

145. L.K. Dyall and J.E. Kemp, Aust. J. Chem., 1967, 20, 1395.

146. L. Pentimalli, Gazzetta, 1964, 94, 458.

147. R.A. Abramovitch, B.W. Cue, J. Amer. Chem. Soc., 1976, 98, 1478.

148. B.B. Corson, Org. Synth., 1936, 16, 28.

149. A.G. Green and F.M. Rowe, J. Chem. Soc., 1912, 101, 2452; ibid, 1913, 103, 897.

150. R.J. Gaughan, J.P. Picard and J.V.R. Kaufmann, J. Amer. Chem. Soc., 1954, 76, 2233.

151. Th. Zincke and Ph. Schwarz, Annalen, 1899, 307, 40.

152. J.M. Prokipak and P.A. Forte, Can. J. Chem., 1970, 48, 3059.

153. Handbook of Chemistry and Physics, Rubber Co., 1965.

154. K.D. Berlin and M. Nagabushanam, J. Org. Chem., 1964, 2056.

155. I.G.M. Campbell, R.C. Cookson, M.B. Hocking and A.N. Hughes, J. Chem. Soc.(C), 1965, 2184.

156. E.H. Braye, Tetrahedron, 1971, 27, 5523.

157. J. Cason, W.N. Baxter, W. De Acetis, J. Org. Chem., 1959, 24, 247.

158. A. Zwierzak, Can. J. Chem., 1967, 2501.

159. Topics in Phosphorus Chemistry, ed. M. Grayson, E.J. Griffith, Wiley, New York, 1967, Vol.5.

160. F. Ramirez, M. Nagabushanam and C.P. Smith, Tetrahedron, 1968, 1785.

161. T. Mukaiyama, T. Fujiwara, Y. Tamura and Y. Yokata, J. Org. Chem., 1964, 29, 2572.

162. Orgno Phosphorus Compounds, ed. Kosolapoff and Maier, Wiley, New York.

163. H.J. Harwood, N.K. Patel, Macromolecules, 1968, 1(3), 233.

164. K. Issleib and S. Hausler, Chem. Ber., 1961, 94, 113.

165. Beilstein, 16, 758.

166. Shell Int. Res. Maatschappij Chem. Abs. 60, 1964, 12055t.

167. M. Grayson, E.J. Griffith, Topics in Phosphorus Chemistry, pp.274-5, Vol.6, Wiley, New York.

168. L.D. Quin, J.P. Gratz, T.P. Barket, J. Org. Chem., 1968, 1034.

169. H. Fritsche, V. Hasserodt and F. Korte, Chem. Ber., 1964, 1988, 97.

170. L.D. Freedmann and G.O. Doak, J. Amer. Chem. Soc., 1952, 3414.

171. F.G. Mann and I.T. Millar, J. Chem. Soc., 1952, 3039.

172. V.V. Korshak, V.A. Zamyatina, A.I. Solomatina, E.I. Fedia, P.V. Petrovski, J. Organometal. Chem., 1969, 17, 201.

173. M. Grayson, and C.E. Farley, J.C.S. Chem. Comm., 1967, 830.

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

175. J. Zuckerman and M. Das, Inorg. Chem., 1971, 1028.

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

177. L.D. Quin, J.P. Gratz and T.P. Burket, J. Org. Chem., 1966, 1034.

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

179. T.H. Chan and K.T. Nwe, Phosphorus, 1974, 3, 225.

180. W. Gerrard, M. Isaacs, G. Machell, K. Smith and P. Wyrdl, J. Chem. Soc., 1953, 1920.

181. J.E. Malowan, D. Ray Martin and P.J. Pizzolato, Inorg. Synth., 1953, 63.

182. Fishwick and Flint, J.C.S. Chem. Comm., 1968, 30.

183. R. Greenhalgh, J.E. Newbery, R. Woodcock and R.F. Hudson, J.C.S. Chem. Comm., 1969, 22.

184. S. Trippet et al., J. Chem. Soc. (D), 1970, 1350.

185. L.D. Quin and D.A. Mathewes, J. Org. Chem., 1964, 29, 834.

186. S. Chan et al., Tetrahedron, 1969, 25, 1097.

187. F. Ramirez et al., J. Org. Chem., 1977, 42(5), 971.

188. P. Haake et al., J. Amer. Chem. Soc., 1973, 95, 8080.

189. S. Trippett, Chem. Abs., 1977, 86, 88980d.

190. Lydia L. Chang, D.B. Denney, D.Z. Denney and R.J. Kazior J. Amer. Chem. Soc., 1977, 99(7), 2293.

191. R.R. Holmes and J.A. Dieters, J. Chem. Res. S. (Synopses), 1977, 4, 92.

192. J.I.G. Cadogan, R.A. North and A.G. Rowley, J. Chem. Res., 1978, 1, 1.

193. J.I.G. Cadogan, N.J. Stewart and N.J. Tweddle, J.C.S. Chem. Comm., 1978, 182.

194. J.I.G. Cadogan, D.S.B. Grace and P.K.G. Hodgson, J. Chem. Res., 1978, 2, 63.

195. F. Ramirez, M. Nowakowski and J.F. Marecek, J. Amer. Chem. Soc., 1977, 99, 4515.

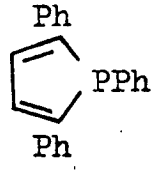
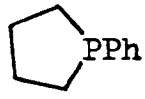
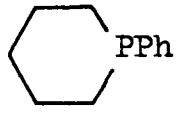
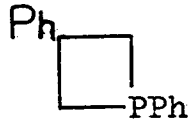
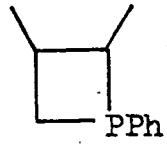
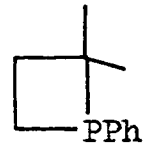
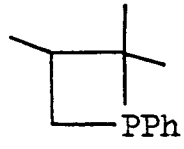
196. R.F. Hudson and R.C. Woodcock, Ann. Chem., 1978, 1, 176.

197. S. Trippett, Organophosphorus Chemistry, 1977, 8, 31.

198. D.J.H. Smith, 'Ylides and Related Compounds', Organophosphorus Chemistry, 1977, 8, 177.

TABLE 1

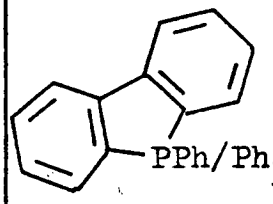
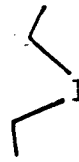
^{1}H N.m.r. thermolysis results[a]

PARENT PHOSPHINE	RATE A	RATE B	% YIELD[b]
	$3.0\times10^{-3}mn^{-1}$ 1*	$3.13\times10^{-3}mn^{-1}$ 2	60-70
	$1.87\times10^{-2}mn^{-1}$ 3	$1.88\times10^{-2}mn^{-1}$ 4	60
	$2.25\times10^{-4}mn^{-1}$ 5	$3.29\times10^{-4}mn^{-1}$ 6	30-35
	$1.57\times10^{-2}mn^{-1}$ 7	$1.19\times10^{-2}mn^{-1}$ 8	60-70
	$1.11\times10^{-1}mn^{-1}$ 9	$1.13\times10^{-1}mn^{-1}$ 10	60-65
	$2.03\times10^{-2}mn^{-1}$ 11	$2.06\times10^{-3}mn^{-1}$ 12	60-68
	$7.8\times10^{-3}mn^{-1}$ 13	$9.6\times10^{-3}mn^{-1}$ 14	60-73

(Continued)

TABLE 1 (Continued)

^{1}H N.m.r. thermolysis results[a]

PARENT PHOSPHINE	RATE A	RATE B	% YIELD[b]
 PPh/Ph_3P	zero	zero	zero
 PPh/$(EtO)_3P$	zero	zero	zero
 PPh (?)	$9.09\times10^{-3}mn^{-1}$ [35]	$8.33\times10^{-3}mn^{-1}$ [36]	50-60

* Numbers in left hand corners correspond with the graph number.

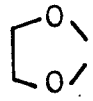
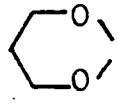
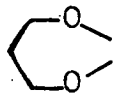
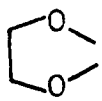
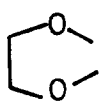
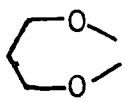
Tables 1-3

a: Rates of formation of 5-substituted-benzofurazans, in BrBz at 160°

b: % Yield of 5-substituted-benzofurazans.

TABLE 2

^{1}H N.m.r. thermolysis results[a]

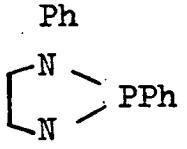
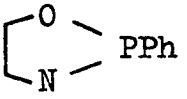
PARENT PHOSPHINE	RATE A	RATE B	% YIELD[b]
 PPh	$1.1\times10^{-3}mn^{-1}$ 15*	$1.02\times10^{-3}mn^{-1}$ 16	60-65
 P-Ph	$2.93\times10^{-3}mn^{-1}$ 17	-	65-70
 $PNMe_2$	$2.36\times10^{-3}mn^{-1}$ 18	-	58-70
 $PNMe_2$	$4.62\times10^{-3}mn^{-1}$ 19	-	63-66
 POMe	$3.0\times10^{-2}mn^{-1}$ 20	$2.9\times10^{-2}mn^{-1}$ 21	55-70
 P-Cl and  P-Cl	no reaction with azide	no reaction with azide	-

* Numbers in left hand corners correspond with graph number.

a,b: see Table 1

TABLE 3

^{1}H N.m.r. thermolysis results[a]

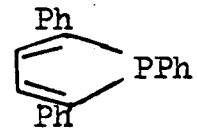
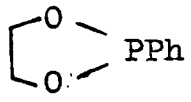
PARENT PHOSPHINE	RATE A	RATE B	% YIELD[b]
	$3.6\times10^{-2}mn^{-1}$ 22*	$3.27\times10^{-2}mn^{-1}$ 23	70-100
	$1.88\times10^{-2}mn^{-1}$ 24	$1.73\times10^{-2}mn^{-1}$ 25	57-65

* Numbers in left hand corners correspond with the graph number.

a,b: see Table 1

TABLE 4

^{31}P N.m.r. thermolysis results[a]

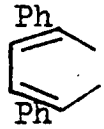
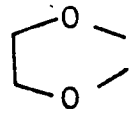
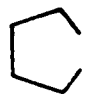
PARENT PHOSPHINE	RATE	INTERMEDIATE
	$7.58 \times 10^{-3} mn^{-1}$ 26*	NO
	$1.63 \times 10^{-3} mn^{-1}$ 27	YES

* Numbers in left hand corners correspond with the graph number.

a: Rates of formation of parent phosphine oxide in BrBz at 160°

TABLE 5

^{31}P N.m.r. hydrolysis results[a]

PARENT PHOSPHINE	RATE A (mol $l^{-1}mn^{-1}$)	RATE B (mol $l^{-1}mn^{-1}$)	RATE C (mol $l^{-1}mn^{-1}$)
	6.24×10^{-4} 28*	7.4×10^{-4} 29	7.27×10^{-4} 30
	6.8×10^{-4} 31	9.7×10^{-4} 32	-
	8.8×10^{-4} 33	1.18×10^{-3} 34	

* Numbers in left hand corners correspond with the graph number.

a: Rates of formation of parent phosphine oxide in dioxan at R.T.

TABLE 6

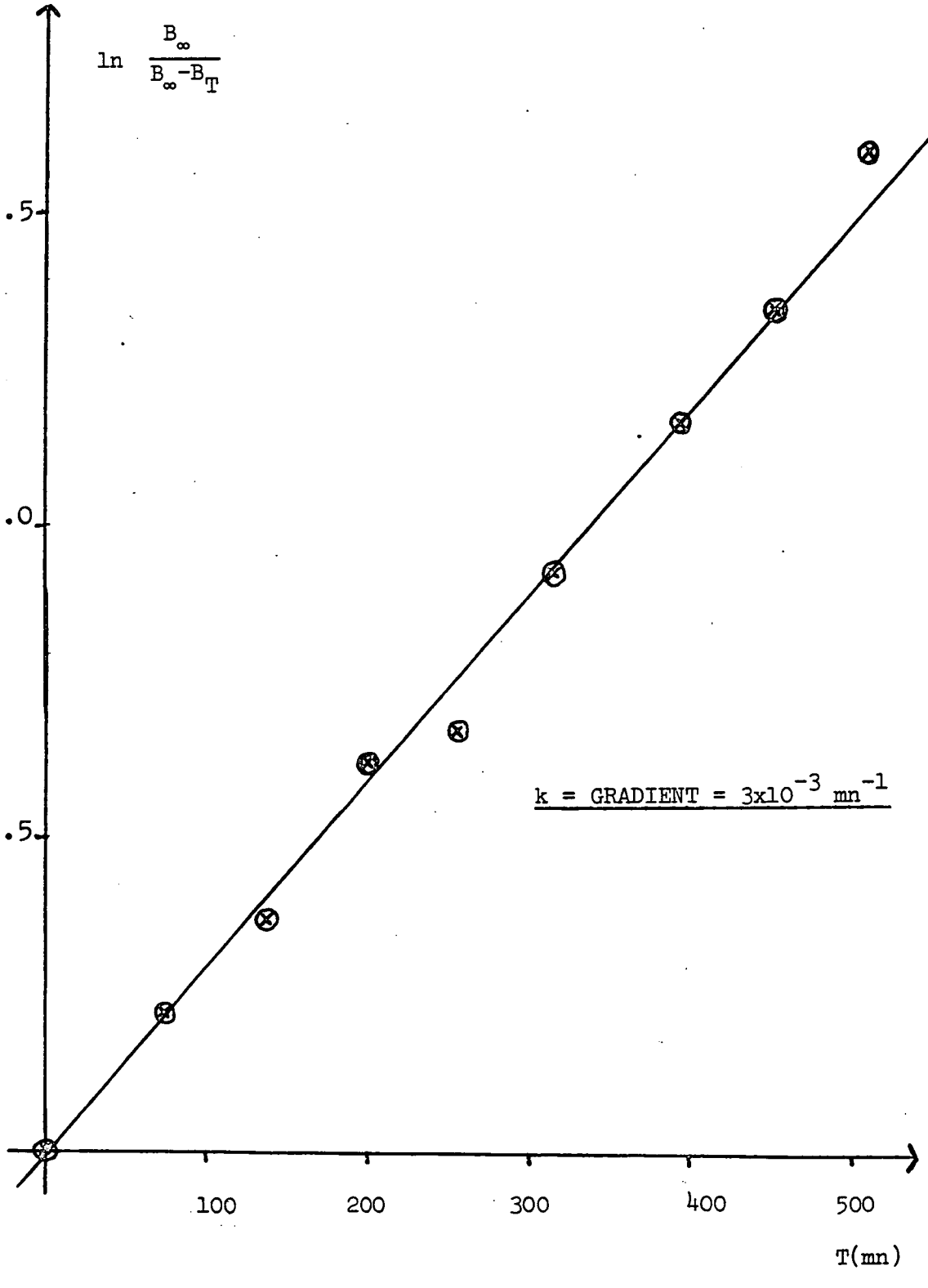
PARENT PHOSPHINE	% ANILINE	AV. % ANILINE	RATIO: ANILINE / OXIDE
1,2*	30 -40	35	.54
3,4	40	40	.66
5,6	65 -70	67	2.03
7,8	30 -40	35	.54
9,10	35 -40	37	.59
11, 12	32 -40	36	.56
13,14	27 -40	34	.52
15,16	35 -40	37	.59
17	30 - 35	33	.50
18	30 -42	36	.56
19	34 -37	36	.56
20,21	30 -45	37	.59
22,23	30 - 0	15	.18
24,25	35 -43	39	.64
35, 36	40 -50	45	.82

* Refers tables 1-5.

Apart from 3 obvious deviations ratio of amine to oxide remains remarkably similar in 0.5 - 0.6 range.

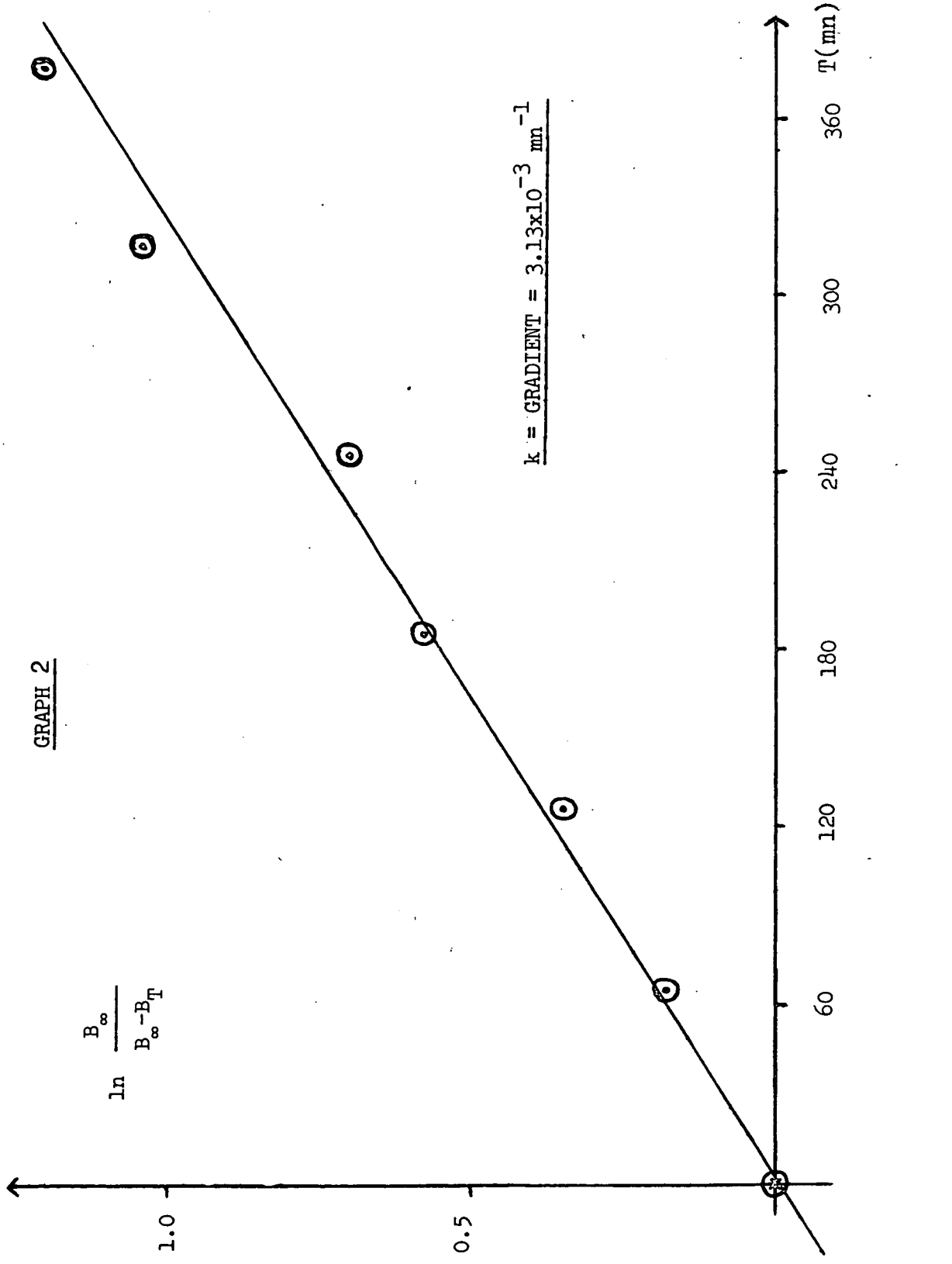
Formation of 5-Methylbenzofurazan from N-(4-Methyl-2-nitrophenyl)-imino-1,2,5-triphenylphosphole

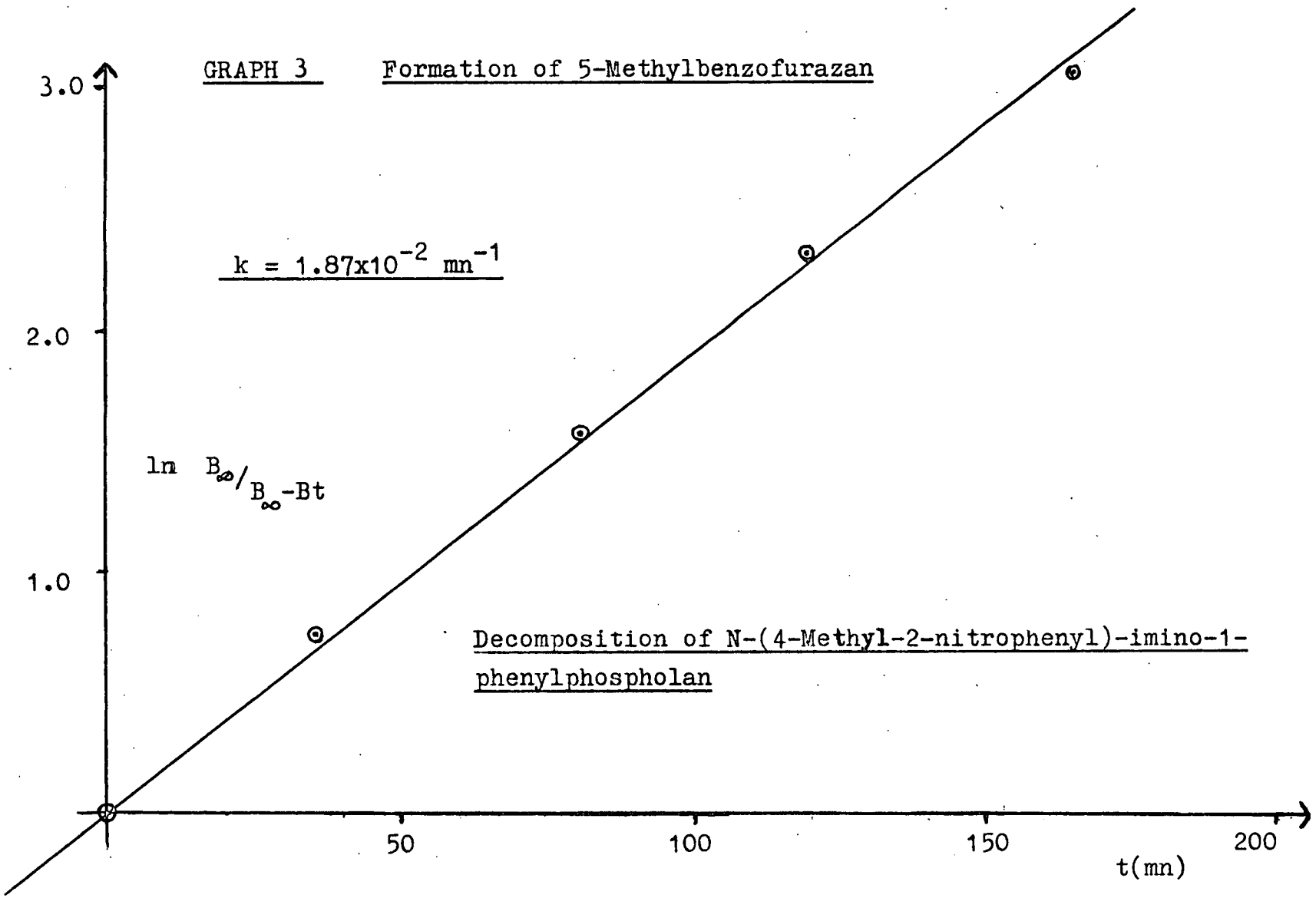
GRAPH 1



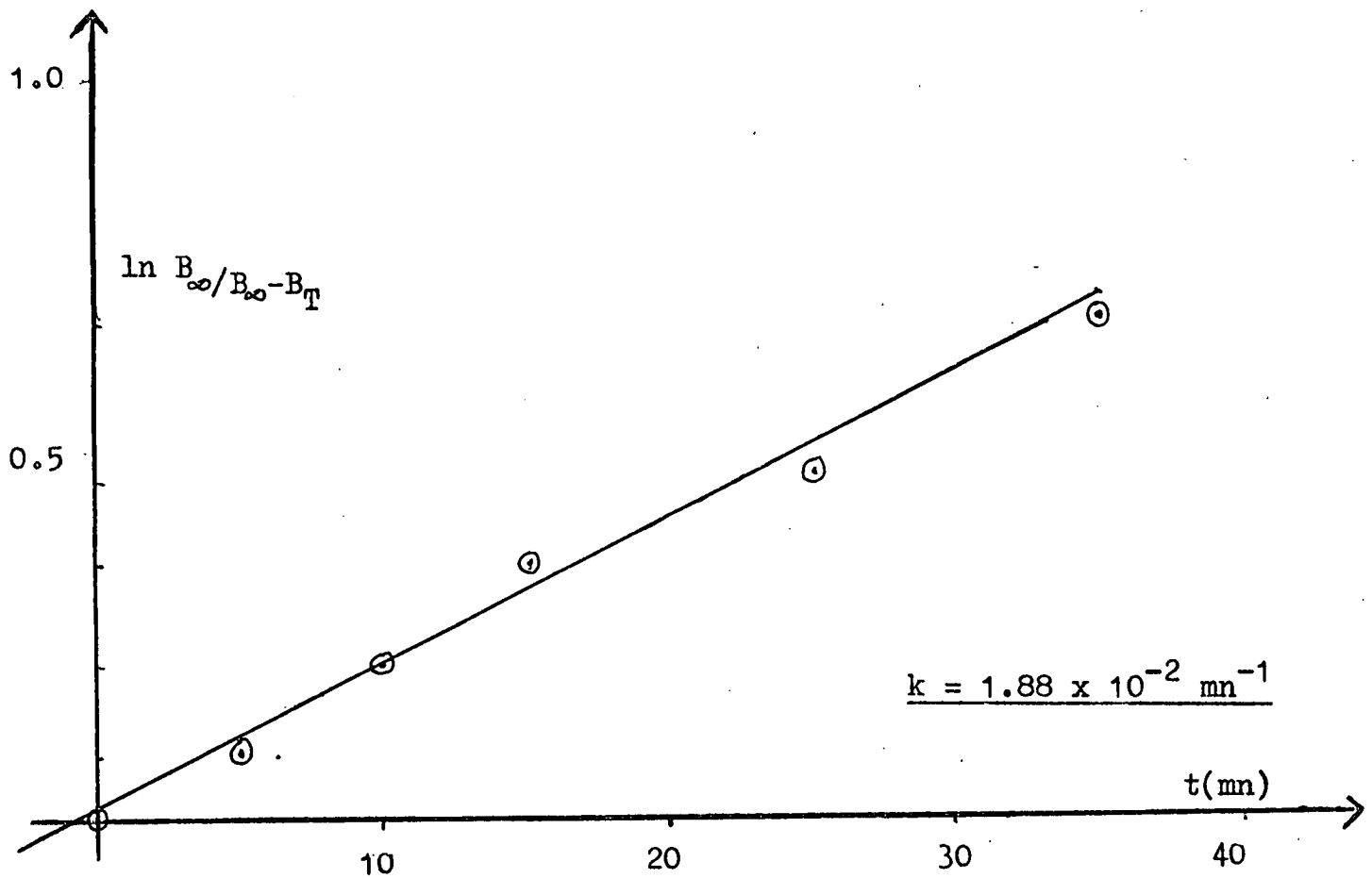
Formation of 5-Methoxybenzofurazan from

N-(4-Methoxy-2-nitrophenyl)-imino-1,2,5-triphenylphosphole



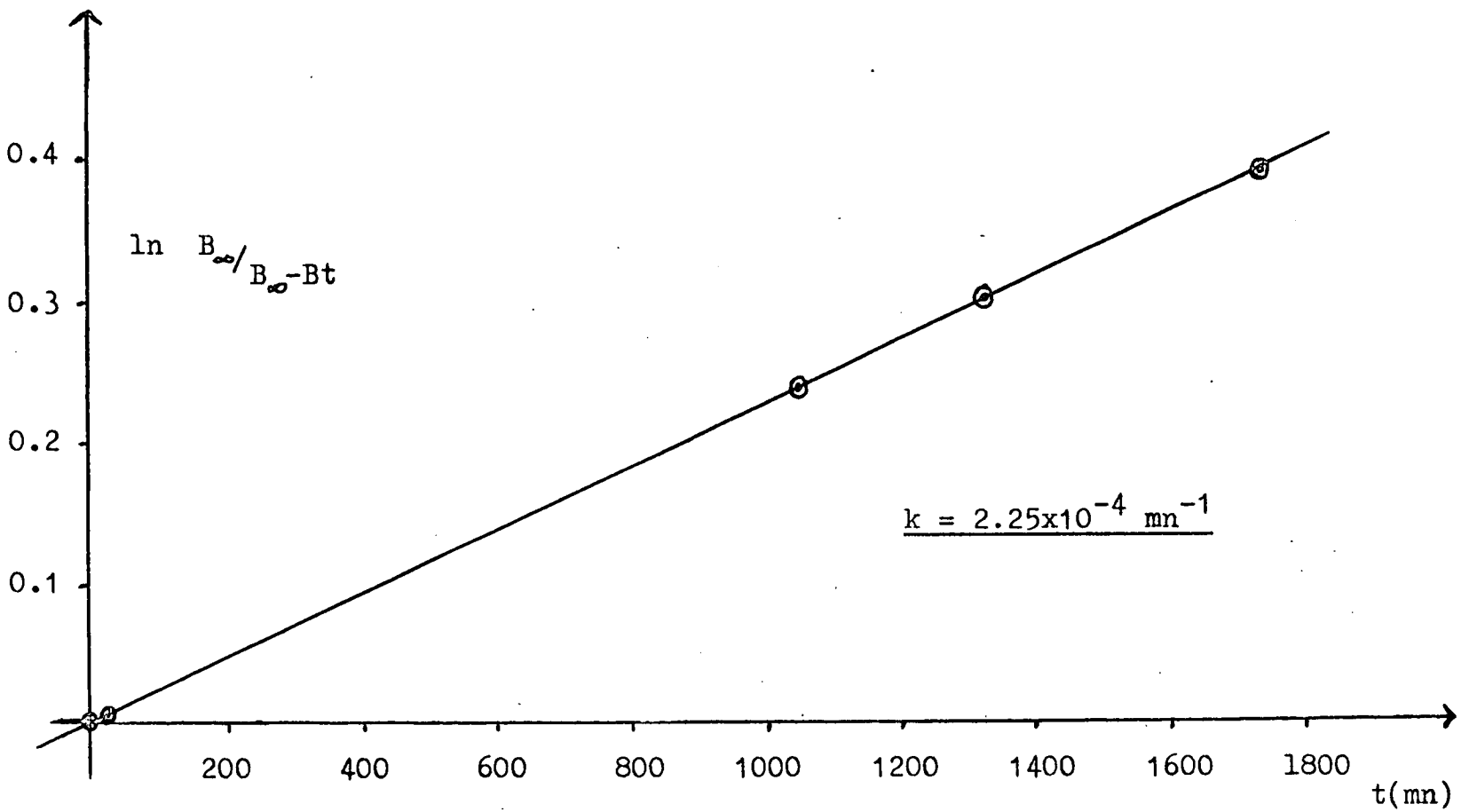

GRAPH 3 Formation of 5-Methylbenzofurazan
k = 1.87x10^{-2} mn^{-1}
3.0
2.0
1.0
ln $B_\infty / B_\infty - Bt$
Decomposition of N-(4-Methyl-2-nitrophenyl)-imino-1-phenylphospholan
50
100
150
200
t(mn)

GRAPH 4 Formation of 5-methylbenzofurazan from N-(4-methyl-2-nitrophenyl)-imino-1-phenylphospholan

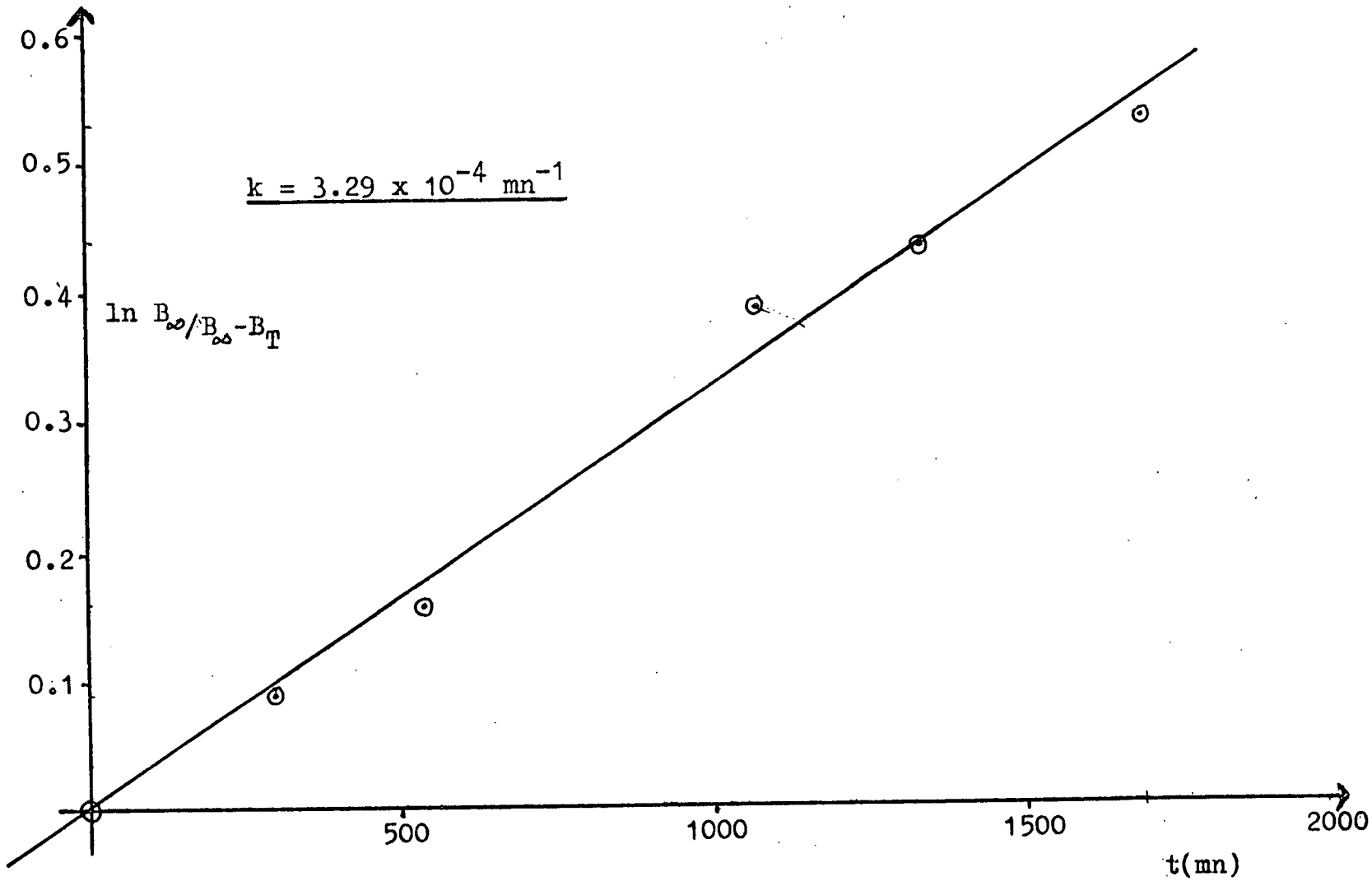


GRAPH 5 Formation of 5-Methylbenzofurazan

Decomposition of N-(4-Methyl-2-**nit**rophenyl)-imino-1-phenylphosphorinan

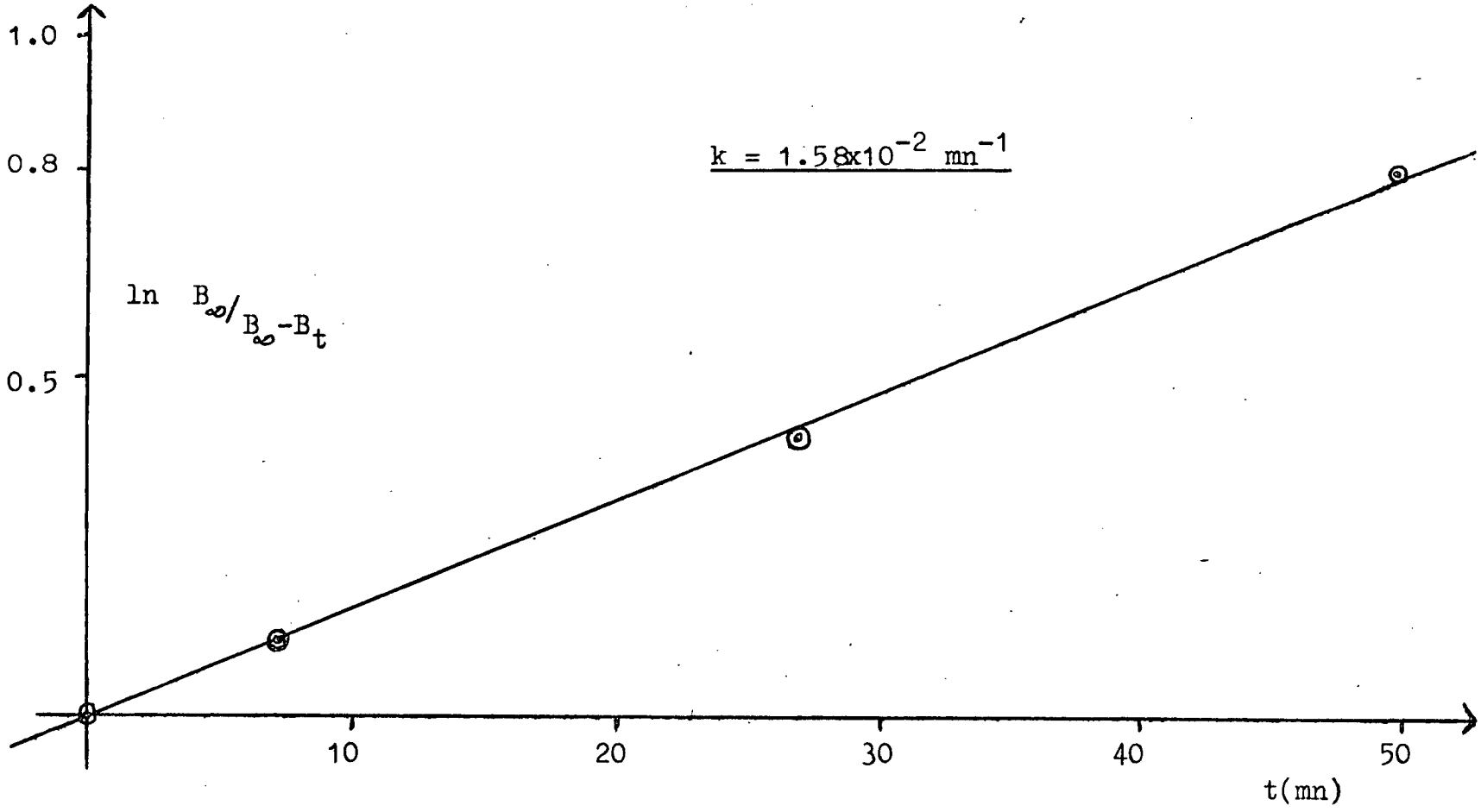


GRAPH 6 Formation of 5-methylbenzofurazan from N-(4-methyl-2-nitrophenyl)-imino-1-phenylphosphorinan



GRAPH 7 Formation of 5-Methylbenzofurazan

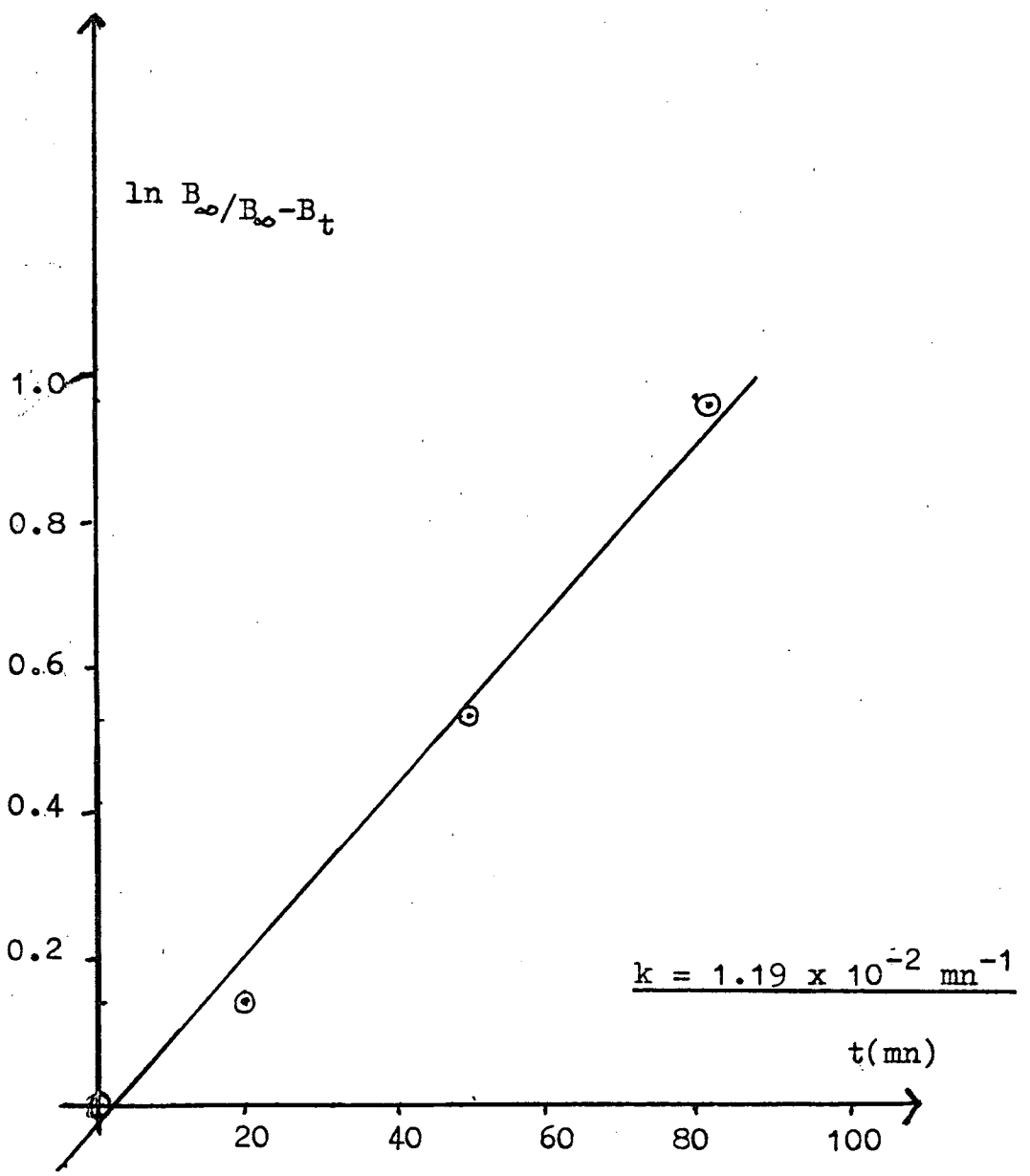
Decomposition of N-(4-Methyl-2-nitrophenyl)-imino-1,3-diphenylphosphetan



GRAPH 8

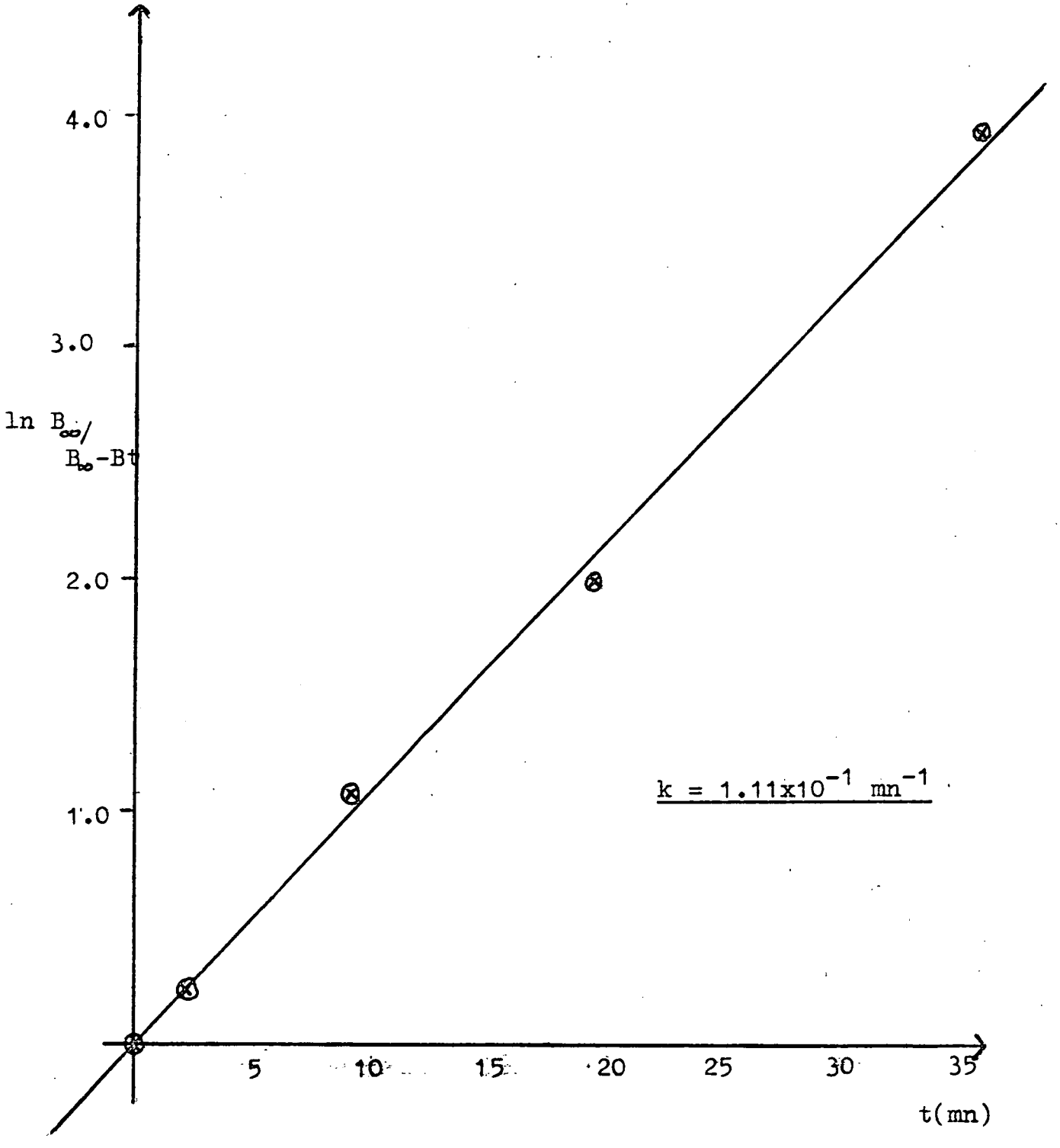
Formation of 5-methylbenzofurazan from

N-(4-methyl-2-nitrophenyl)-imino-1-3,diphenylphosphetan



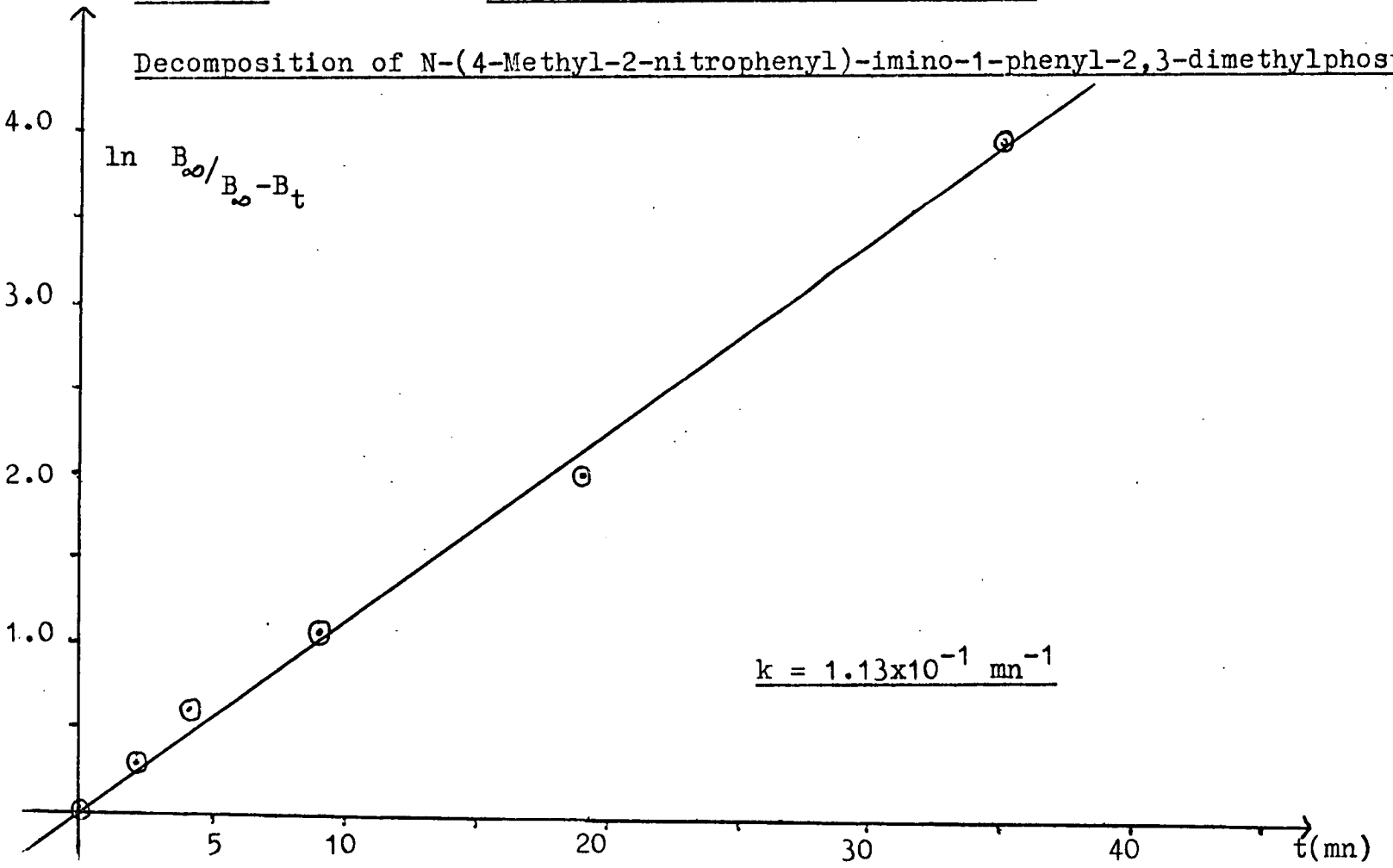
GRAPH 9

Decomposition of N-(4-methyl-2-nitrophenyl)-imino-1-phenyl-2,3-dimethylphosphetan - formation of 5-methylbenzofurazan



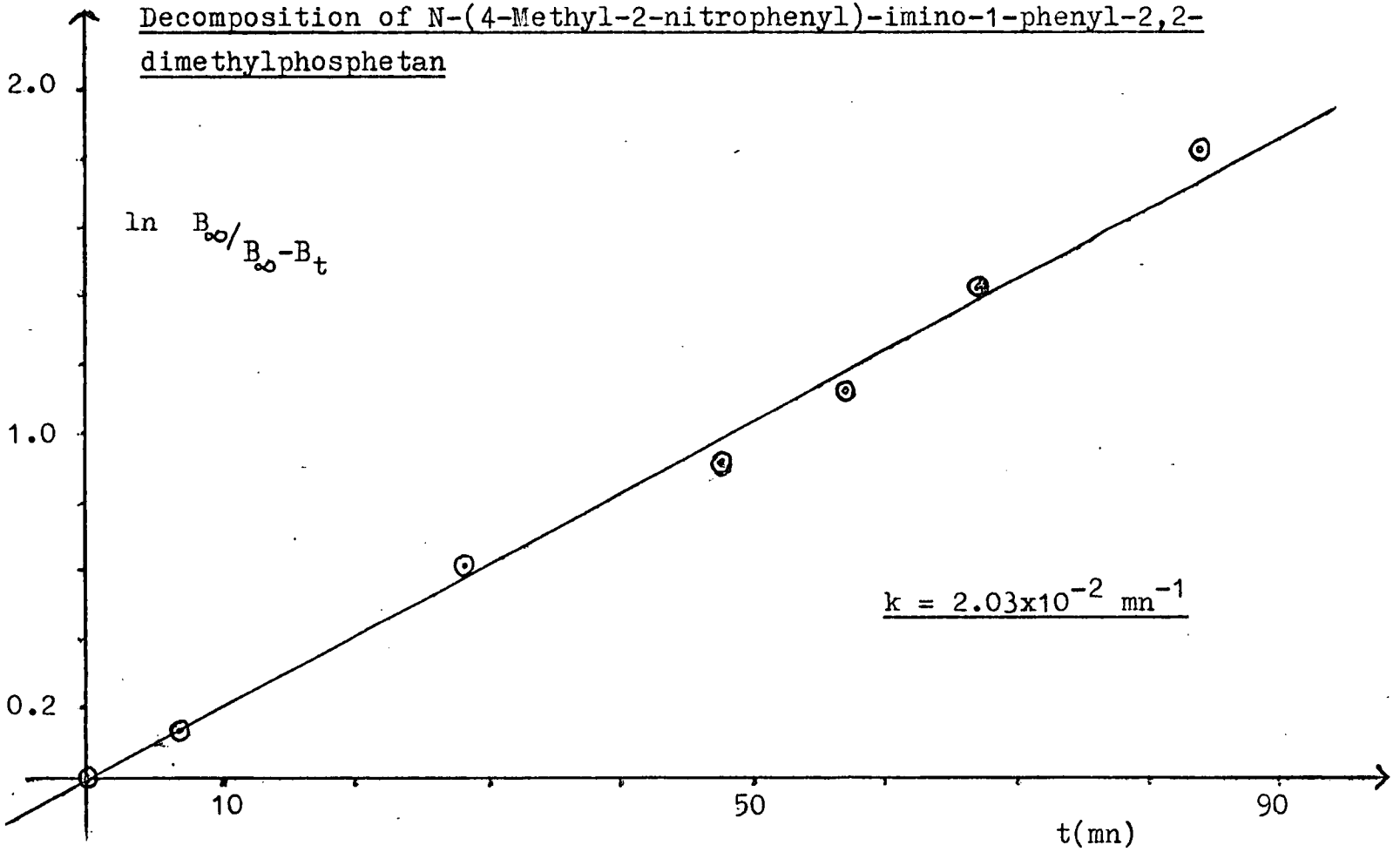
GRAPH 10 Formation of 5-Methylbenzofurazan

Decomposition of N-(4-Methyl-2-nitrophenyl)-imino-1-phenyl-2,3-dimethylphosphetan



GRAPH 11

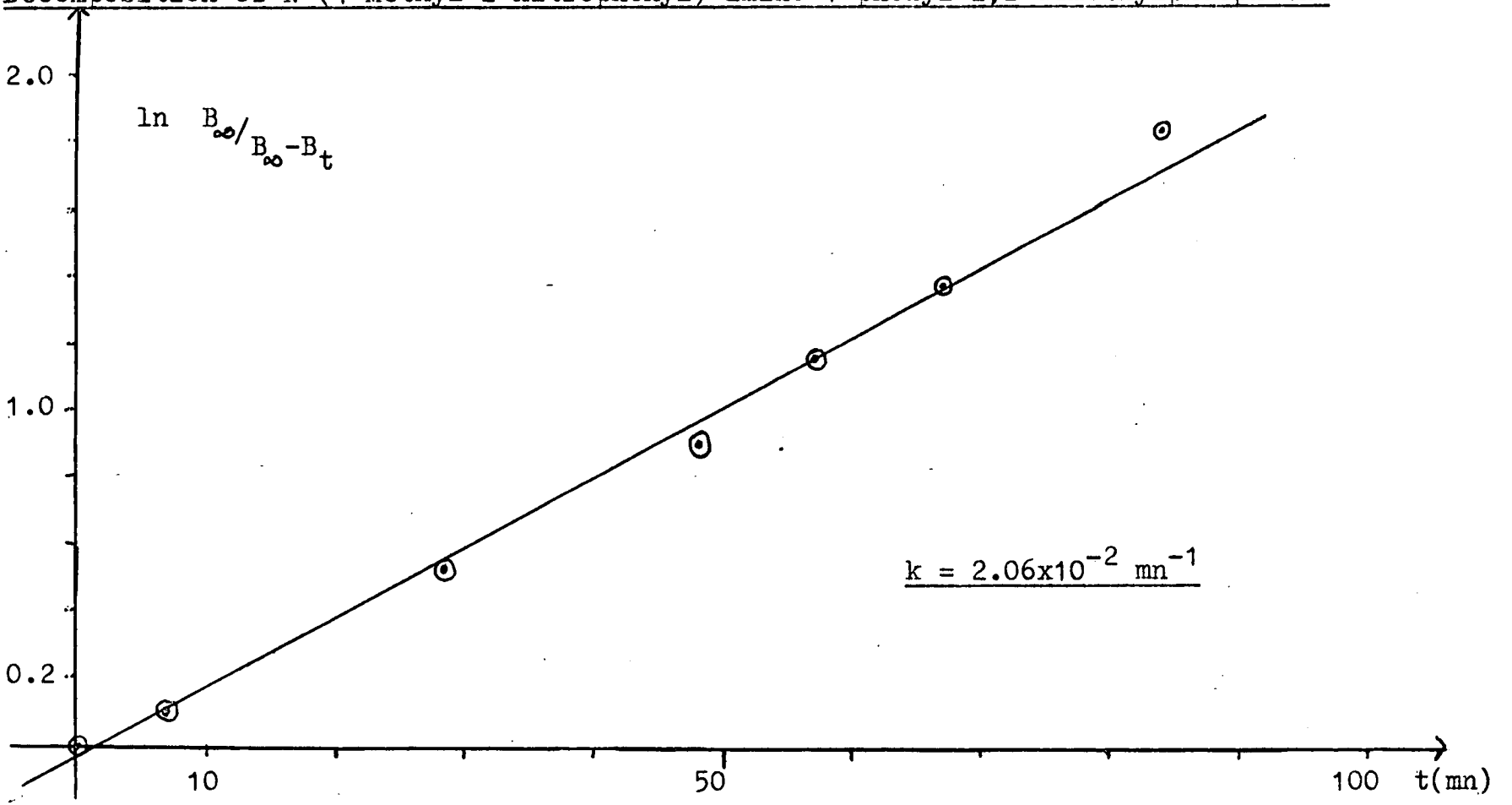
Formation of 5-Methylbenzofurazan



GRAPH 12

Formation of 5-Methylbenzofurazan

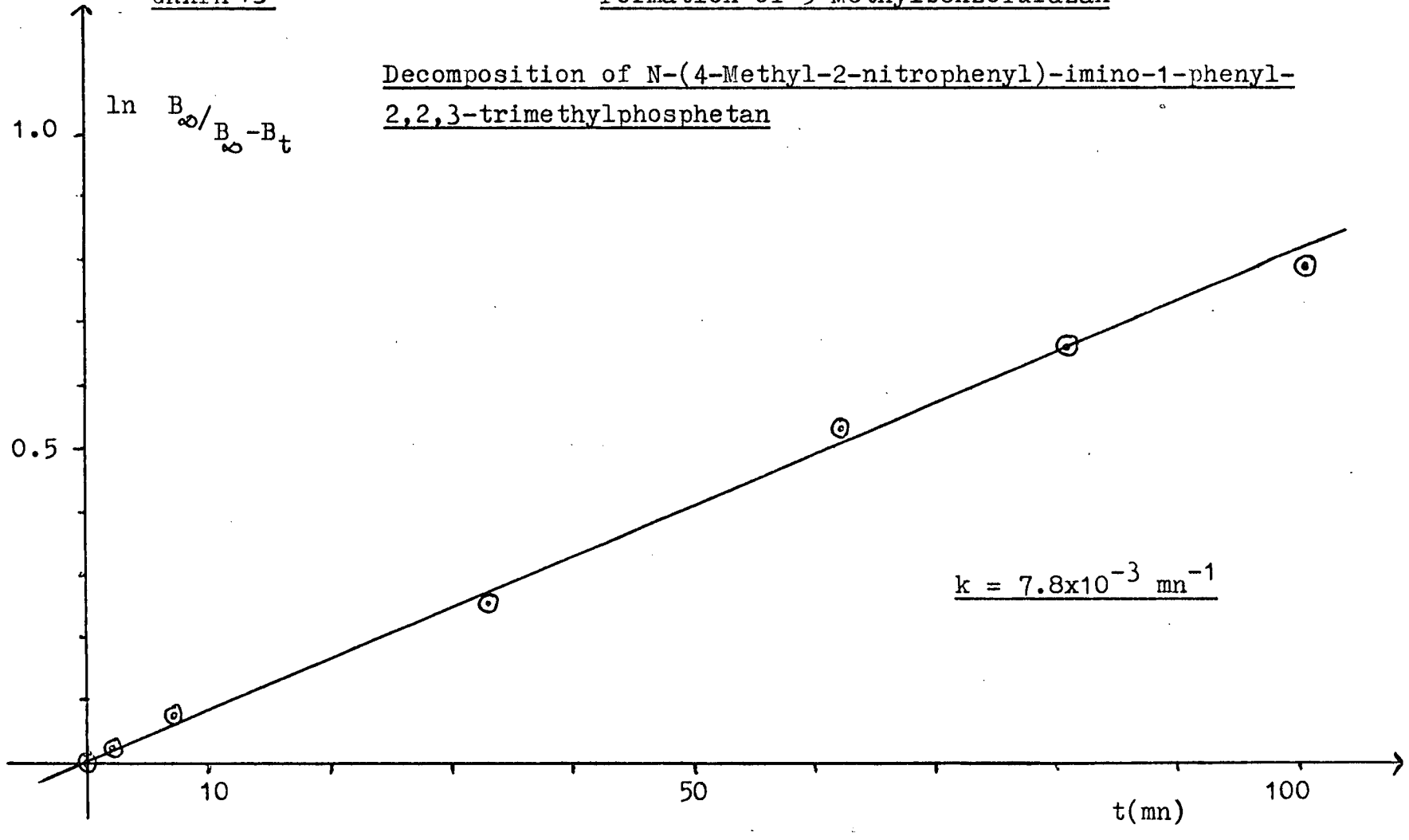
Decomposition of N-(4-Methyl-2-nitrophenyl)-imino-1-phenyl-2,2-dimethylphosphetan



GRAPH 13

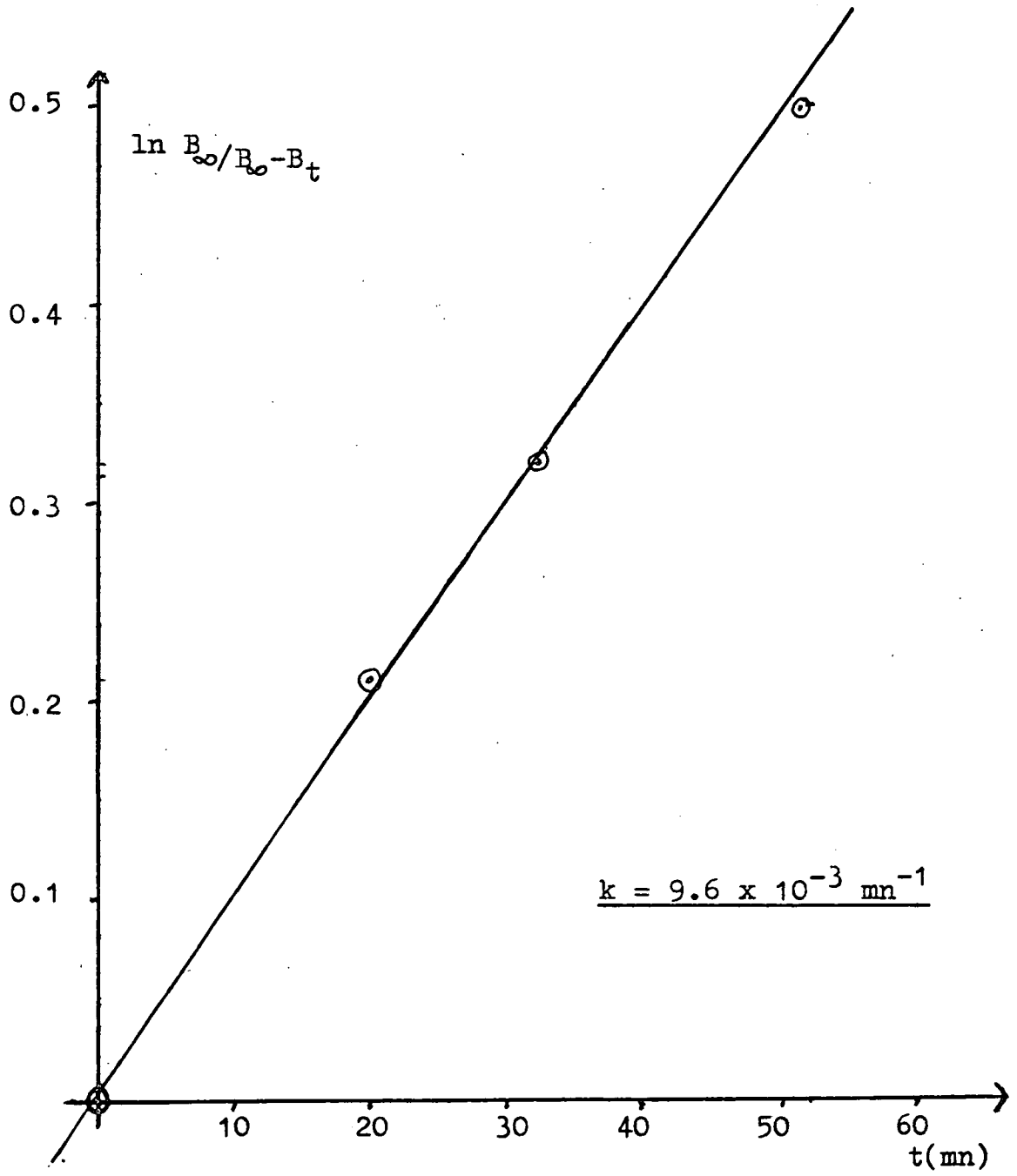
Formation of 5-Methylbenzofurazan

Decomposition of N-(4-Methyl-2-nitrophenyl)-imino-1-phenyl-2,2,3-trimethylphosphetan



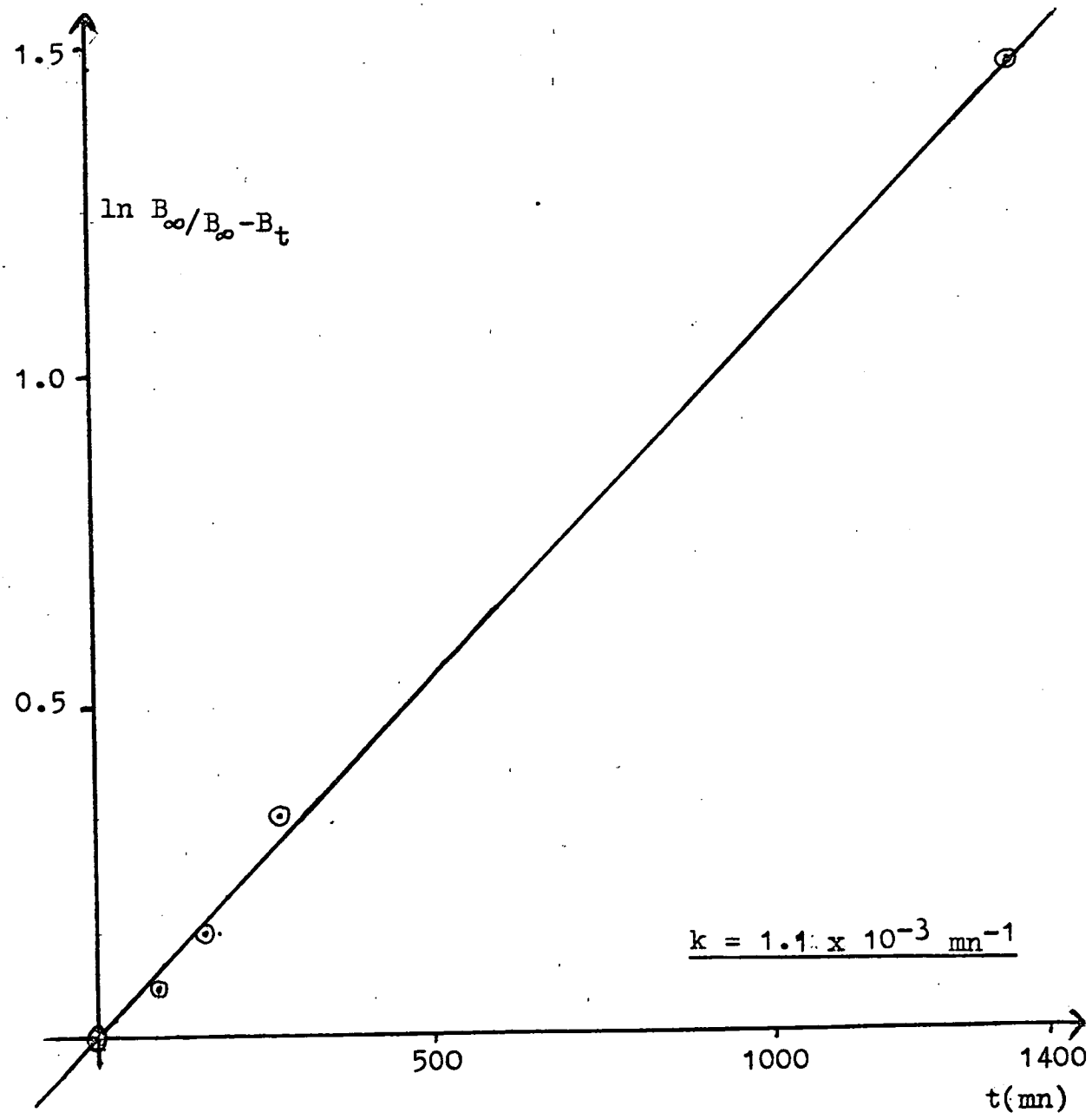
GRAPH 14

Formation of 5-methoxybenzofurazan from N-(4-methoxy-2-nitrophenyl)-imino-1-phenyl-2,2,3-trimethylphosphetan



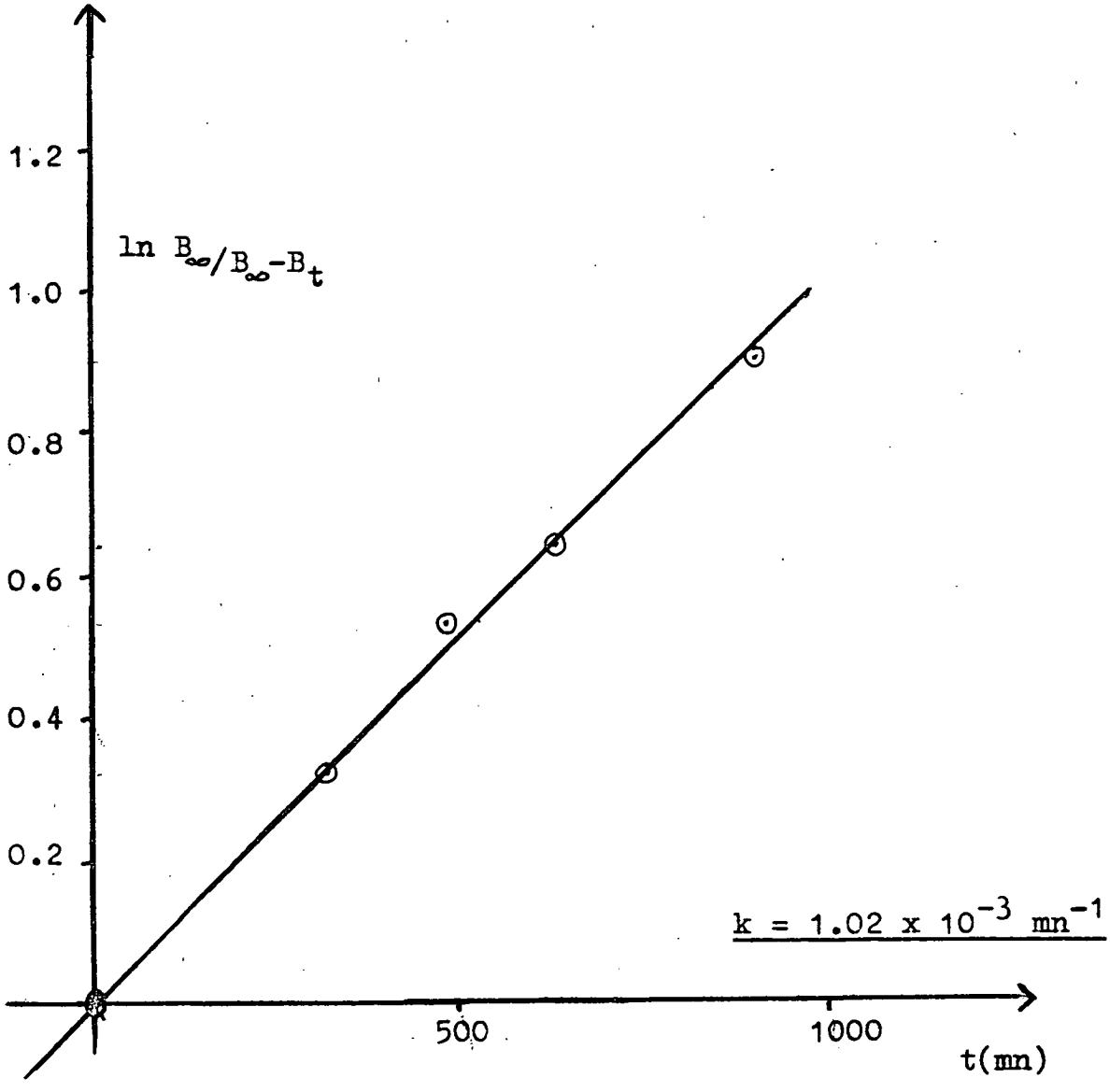
GRAPH 15

Formation of 5-methylbenzofurazan from N-(4-methyl-2-nitrophenyl)-imino-1-phenyl--1.3.2-dioxaphospholan



GRAPH 16

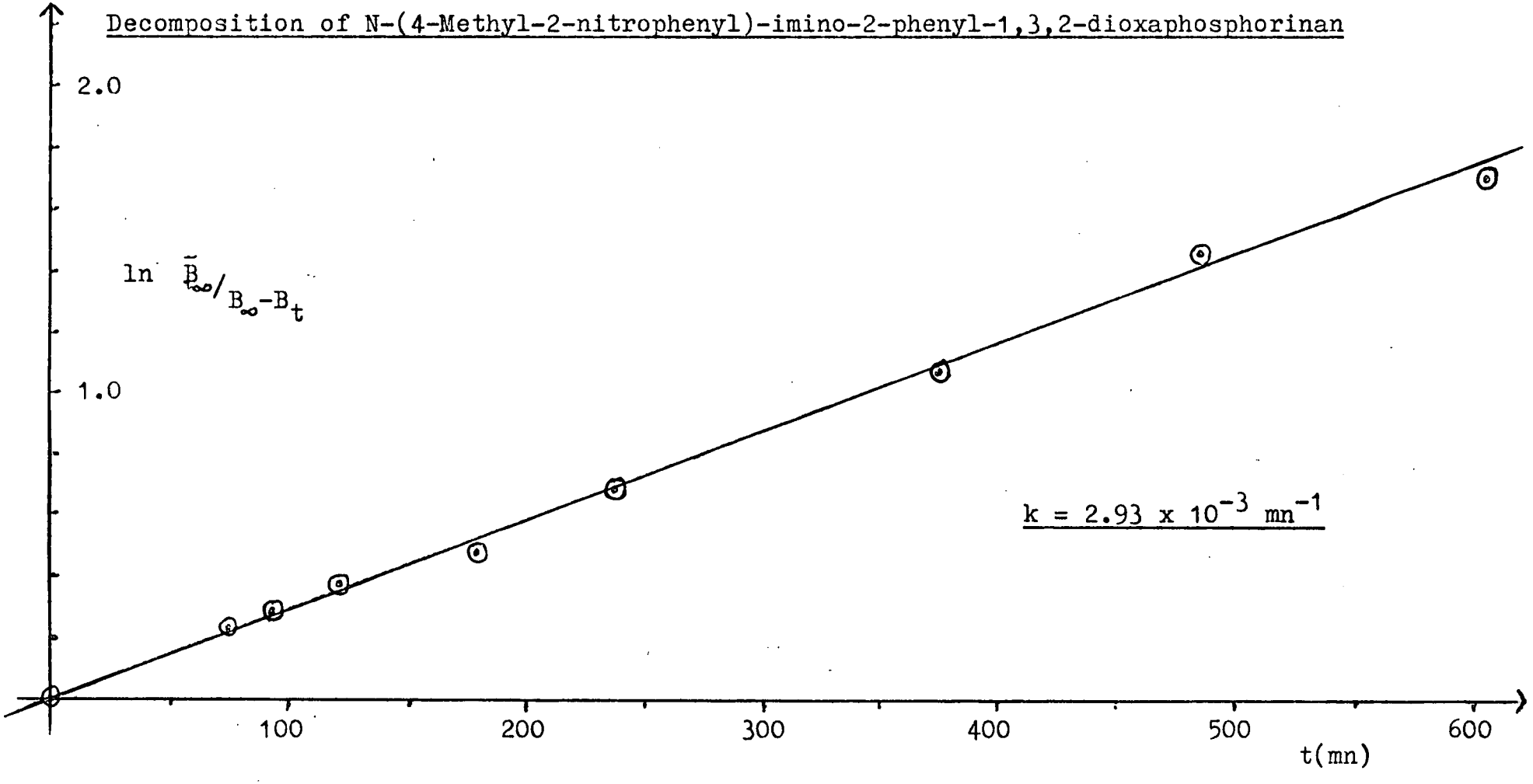
Formation of 5-methylbenzofurazan from N-(4-methyl-2-nitrophenyl)-imino-1-phenyl--1,3,2-dioxaphospholan



GRAPH 17

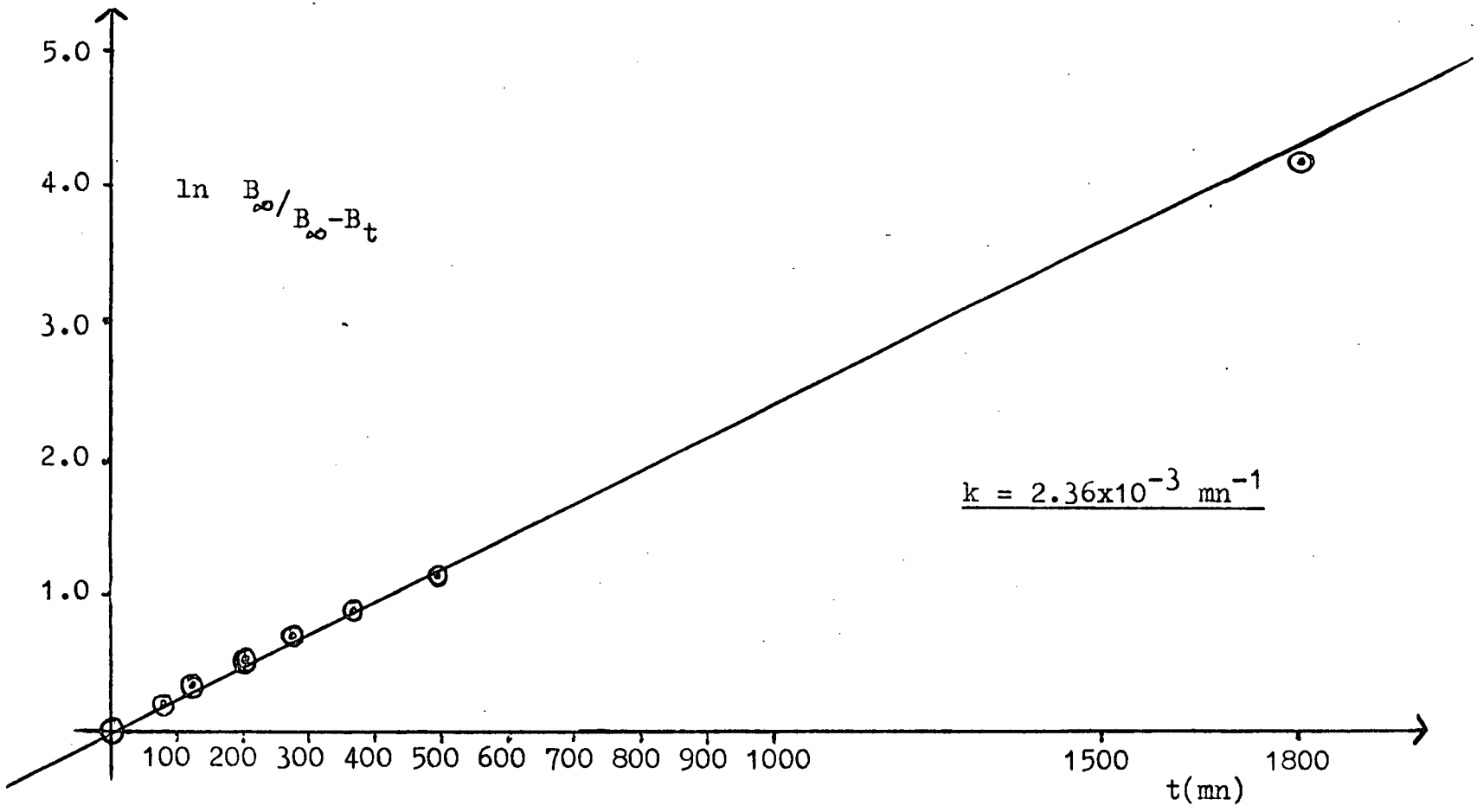
Formation of 5-Methylbenzofurazan

Decomposition of N-(4-Methyl-2-nitrophenyl)-imino-2-phenyl-1,3,2-dioxaphosphorinan



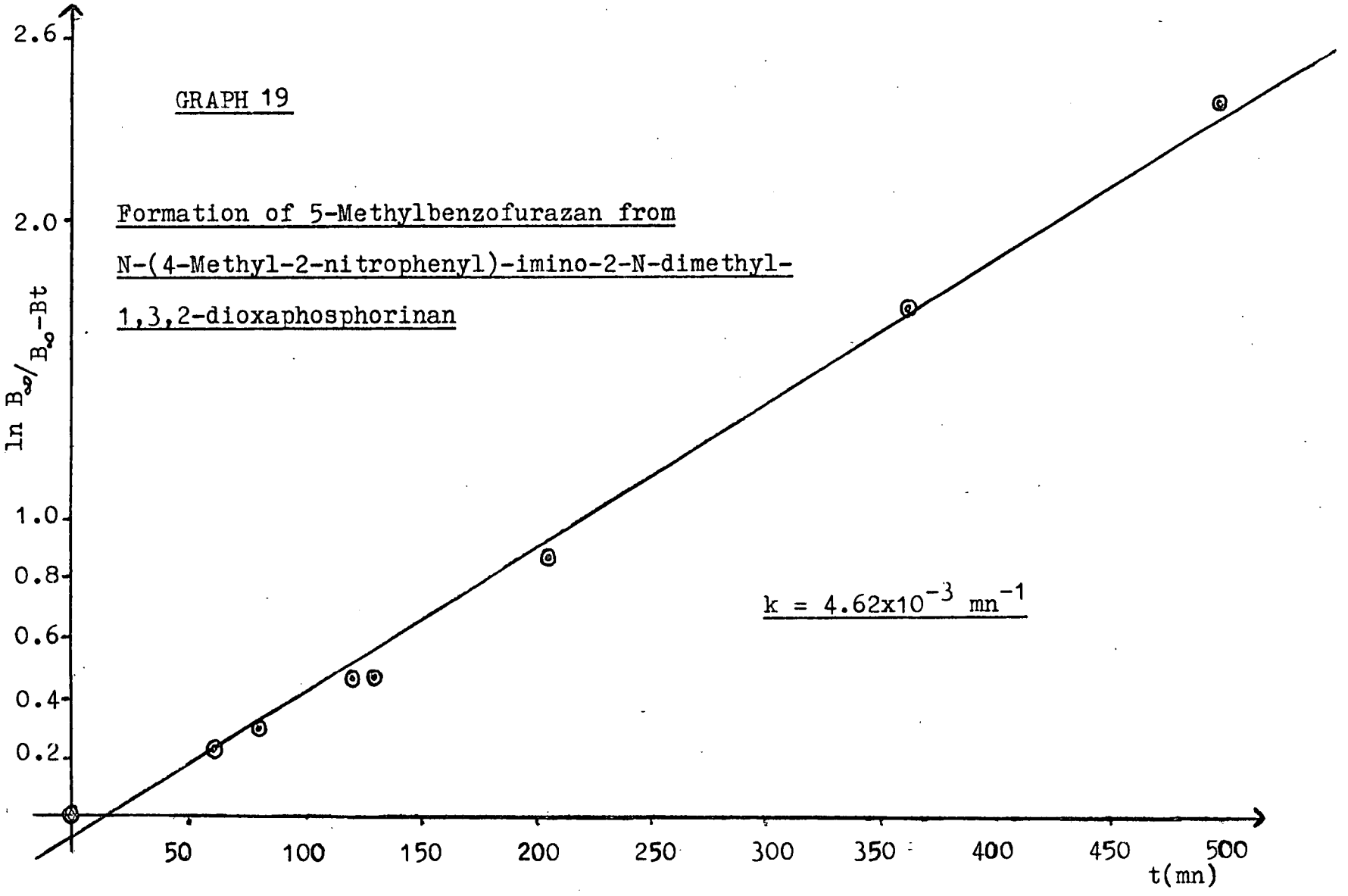
GRAPH 18 Formation of 5-Methylbenzofurazan

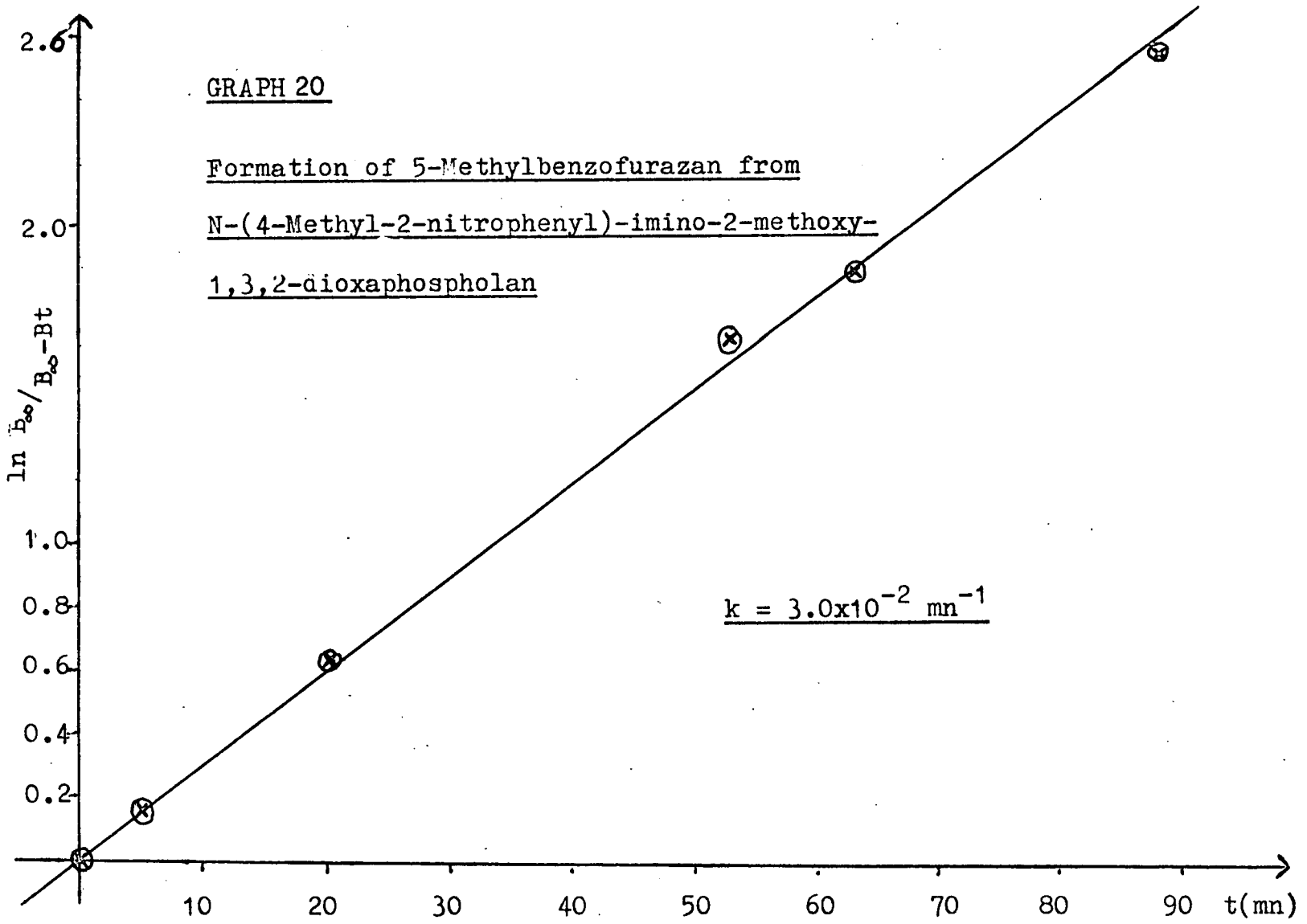
Decomposition of N-(4-Methyl-2-nitrophenyl)-imino-2-N-dimethyl-1,3,2-dioxaphospholan



GRAPH 19

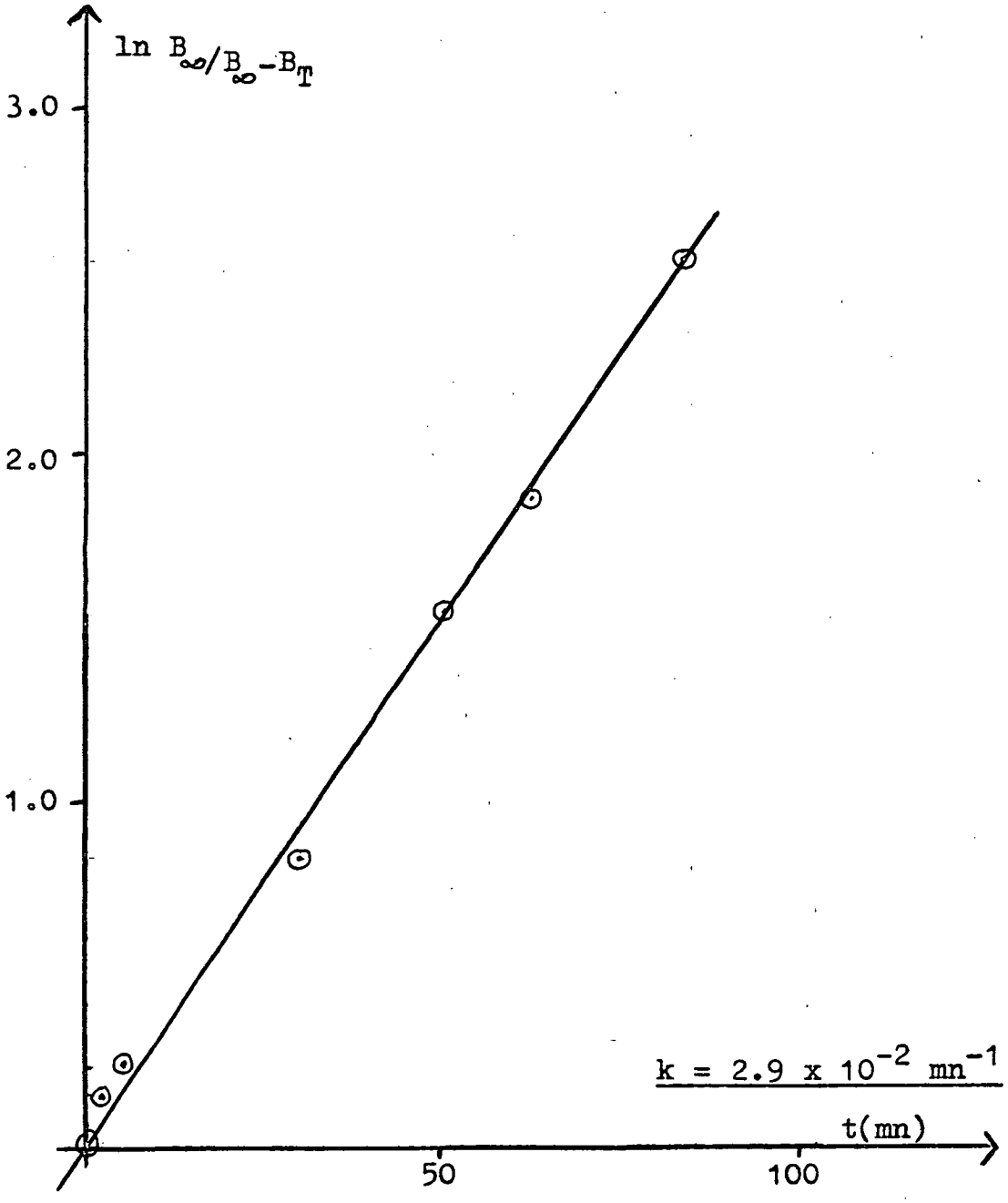
Formation of 5-Methylbenzofurazan from N-(4-Methyl-2-nitrophenyl)-imino-2-N-dimethyl-1,3,2-dioxaphosphorinan




GRAPH 20
Formation of 5-Methylbenzofurazan from
N-(4-Methyl-2-nitrophenyl)-imino-2-methoxy-
1,3,2-dioxaphospholan
k = 3.0x10^-2 mn^-1
ln B∞/B∞-Bt
2.6
2.0
1.0
0.8
0.6
0.4
0.2
10
20
30
40
50
60
70
80
90
t(mn)

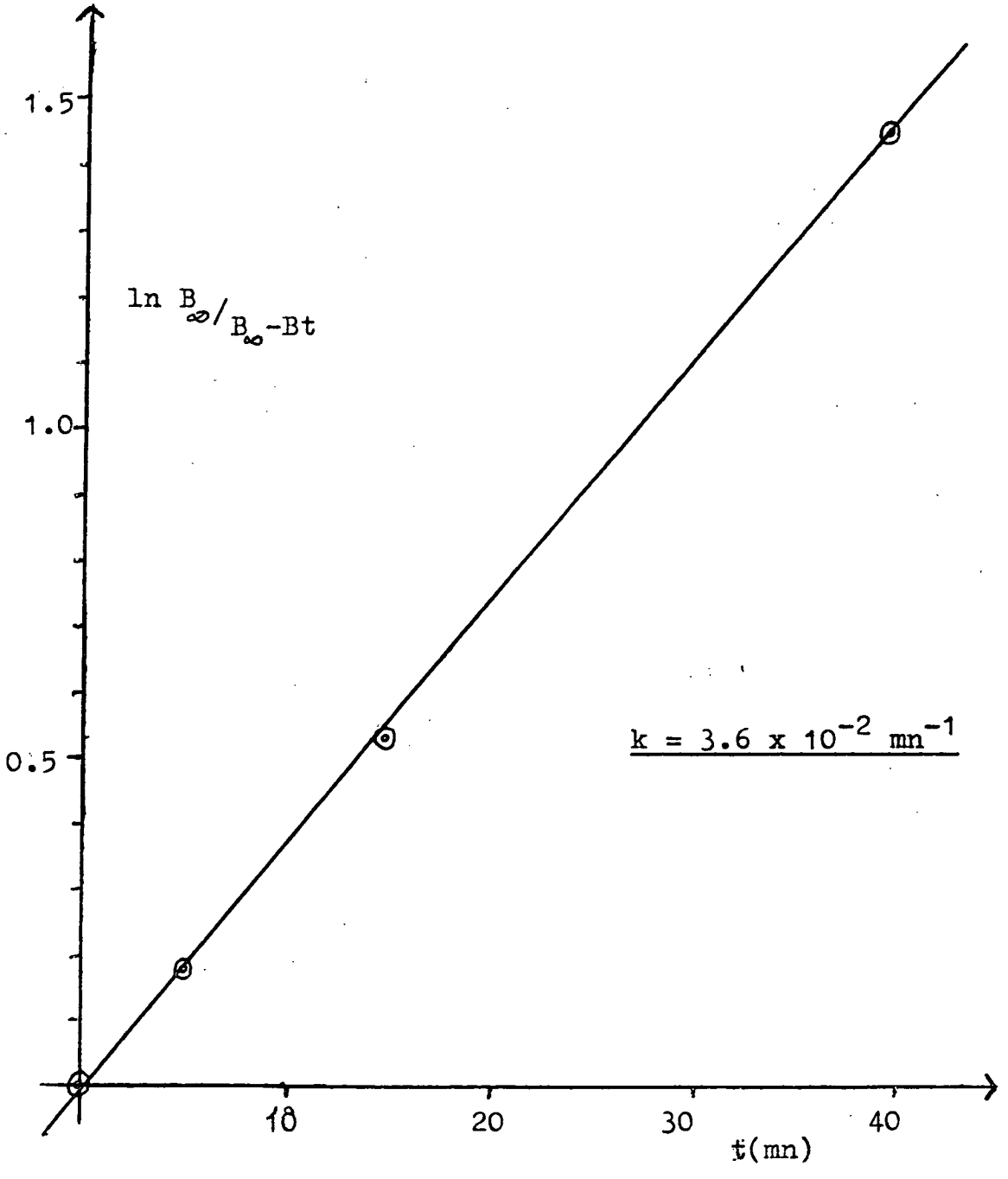
GRAPH 21

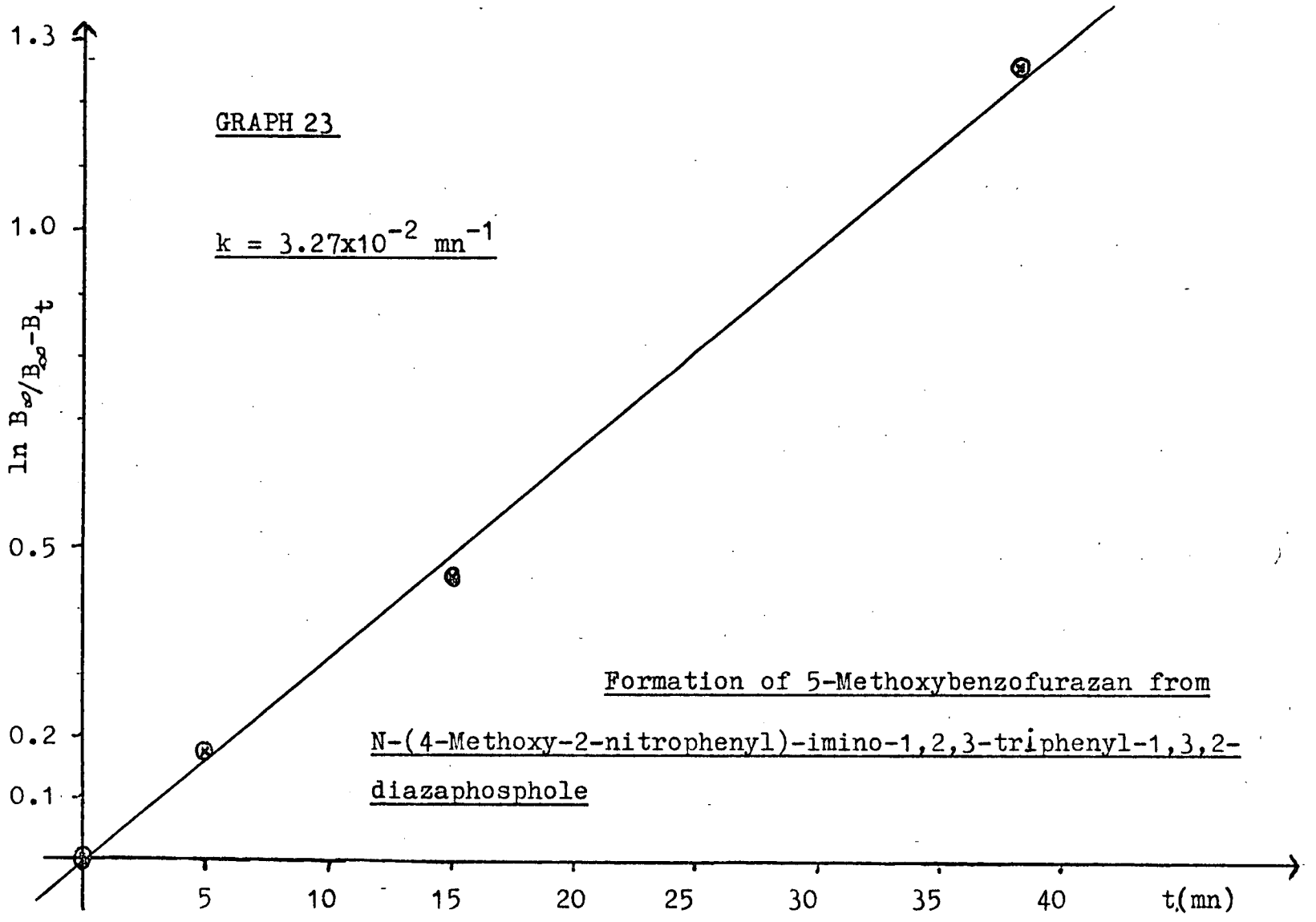
Formation of 5-methylbenzofurazan from N-(4-methyl-2-nitrophenyl)-imino-2-methoxy 1,3,2-dioxaphospholan



GRAPH 22

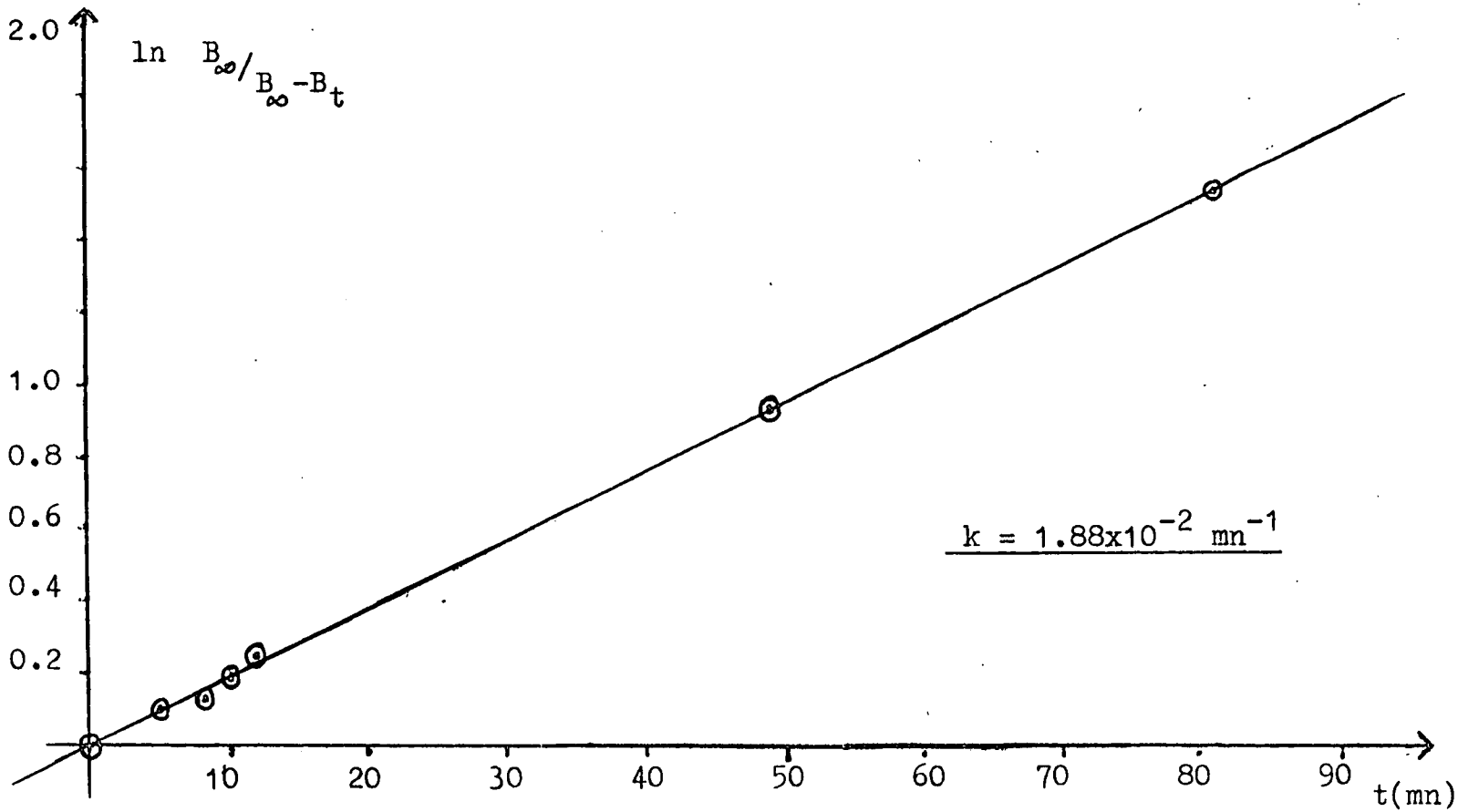
Formation of 5-Methoxybenzofurazan from N-(4-Methoxy-2-nitrophenyl)-imino-1,2,3-triphenyl-1,3,2-diazaphosphole




GRAPH 23
k = 3.27x10^{-2} mn^{-1}
Formation of 5-Methoxybenzofurazan from
N-(4-Methoxy-2-nitrophenyl)-imino-1,2,3-triphenyl-1,3,2-diazaphosphole
ln $B_\infty/B_\infty - B_t$
1.3
1.0
0.5
0.2
0.1
5
10
15
20
25
30
35
40
t(mn)

GRAPH 24 Formation of 5-Methylbenzofurazan

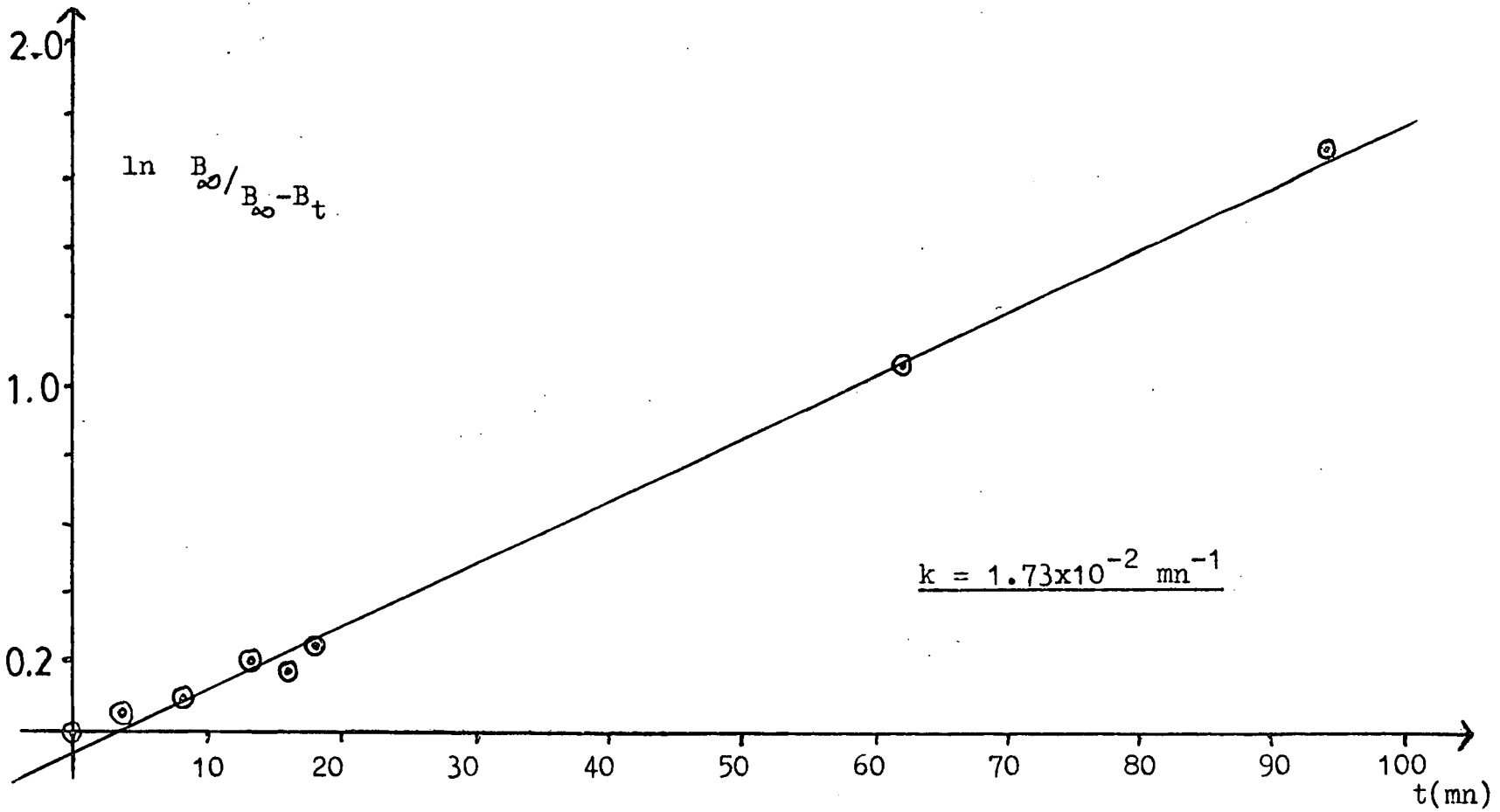
Decomposition of N-(4-Methyl-2-nitrophenyl)-imino-2-phenyl-3-methyl-1,3,2-oxazaphospholan



GRAPH 25

Formation of 5-Methylbenzofurazan

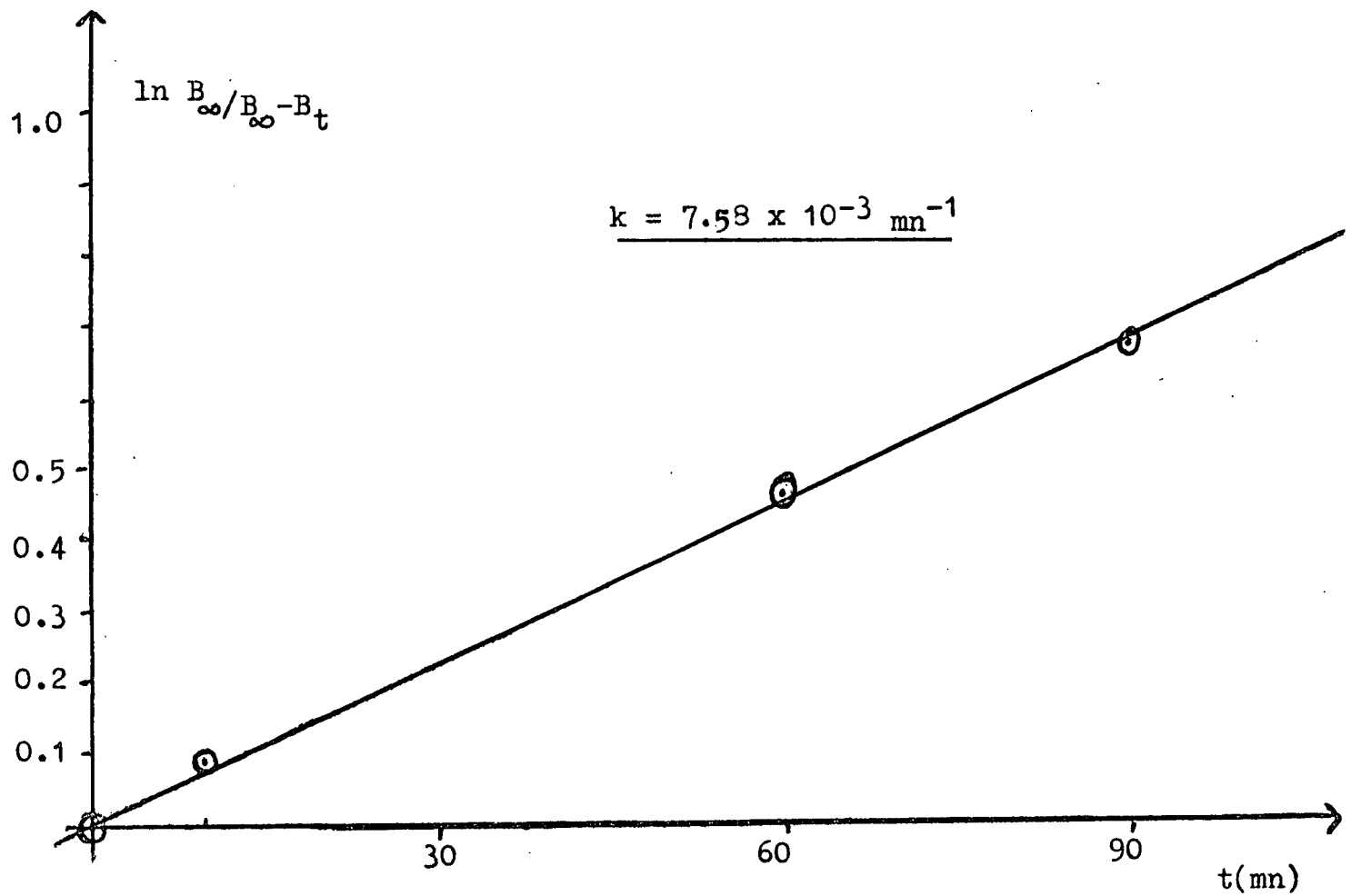
Decomposition of N-(4-Methyl-2-nitrophenyl)-imino-2-phenyl-3-methyl-1,3,2-oxazaphospholan



GRAPH 26

^{31}P N.m.r. thermolysis of N-(4-methyl-2-nitrophenyl)-imino-1,2,5-triphenylphosphole

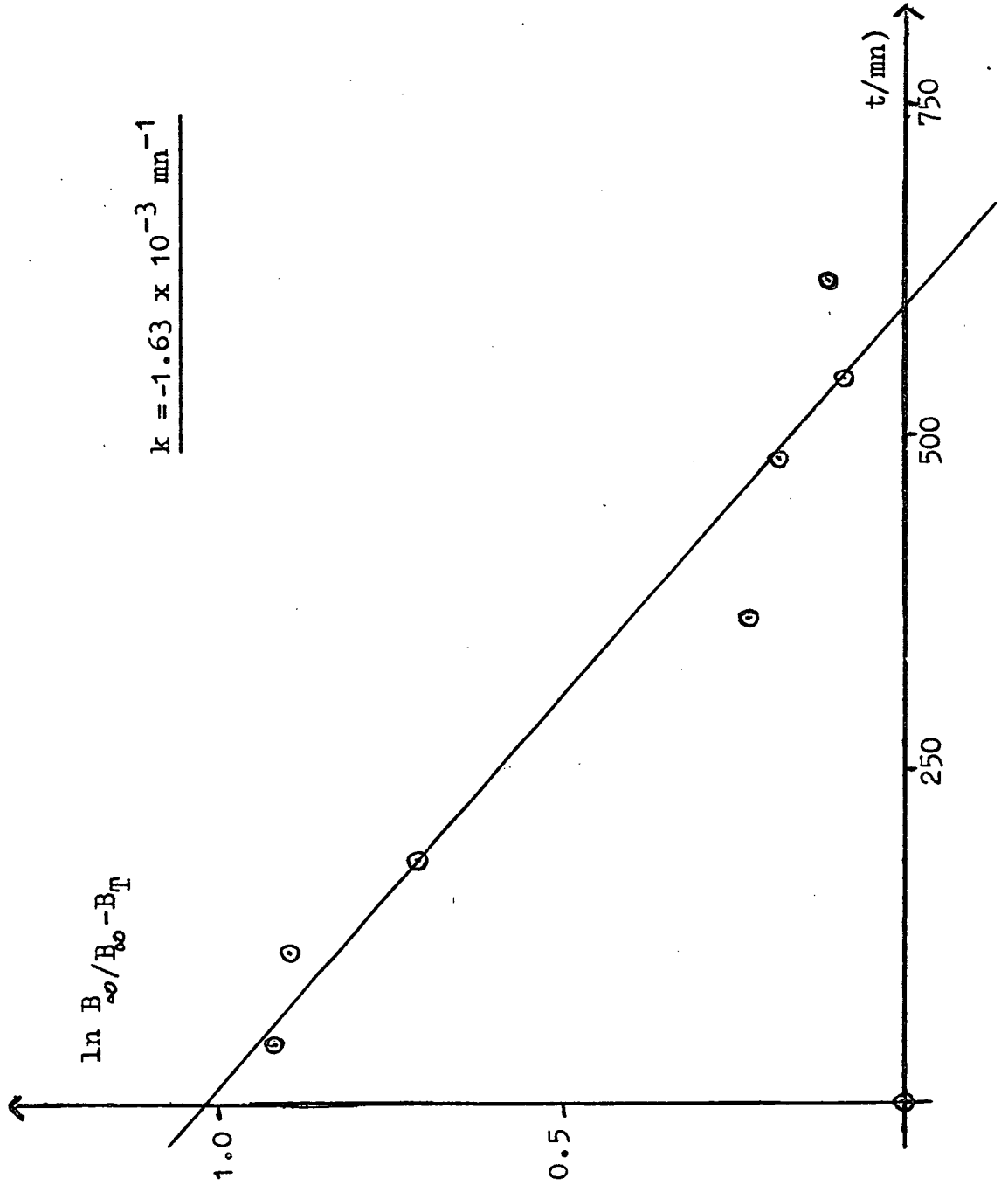
Formation of 1,2,5-triphenylphosphole oxide



$k = 7.58 \times 10^{-3}\ mn^{-1}$

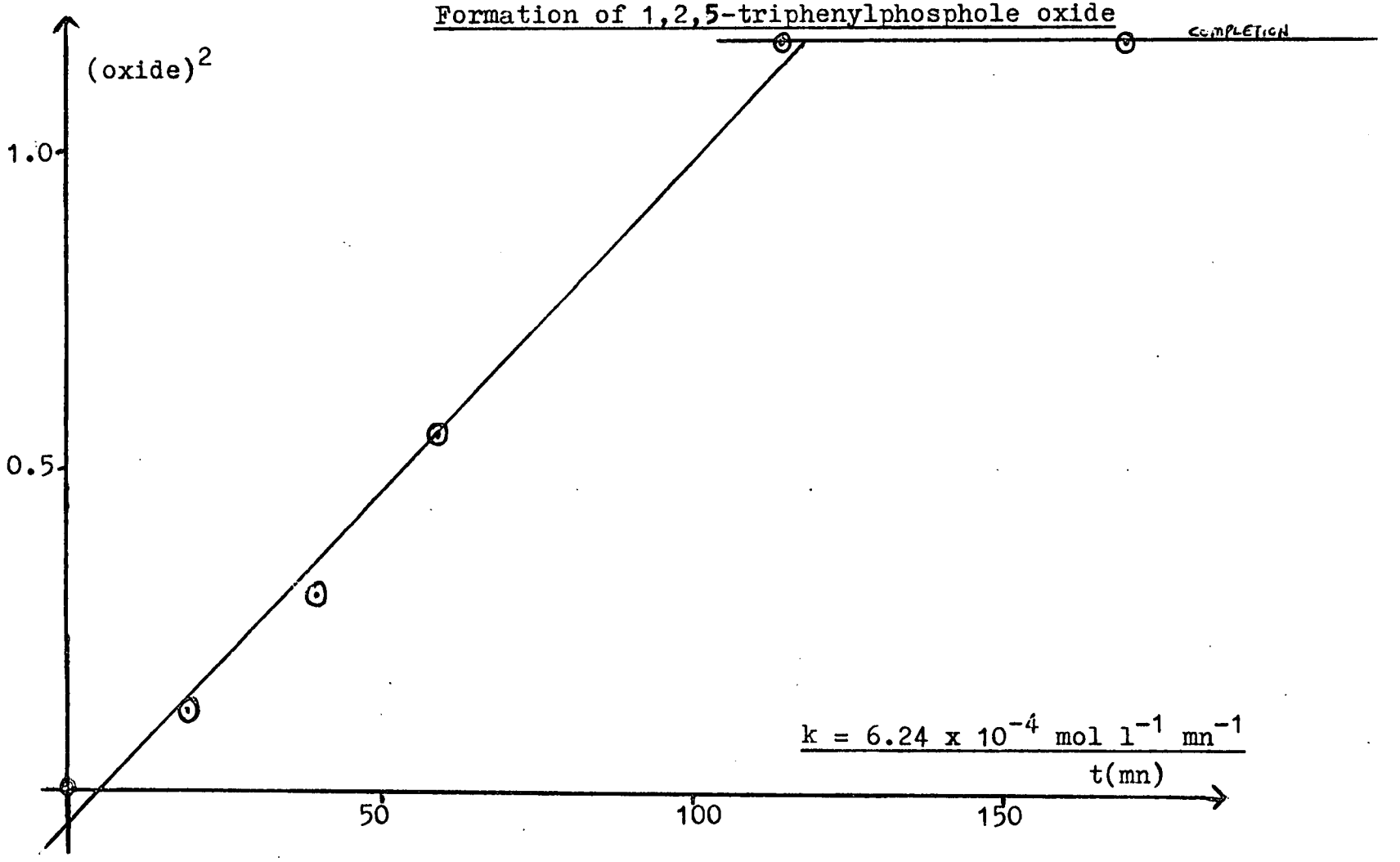
GRAPH 27 ^{31}P N.m.r. thermolysis study

Decomposition of N-(4-methyl-2-nitrophenyl)-imino--2-phenyl-1,3,2-dioxaphospholan



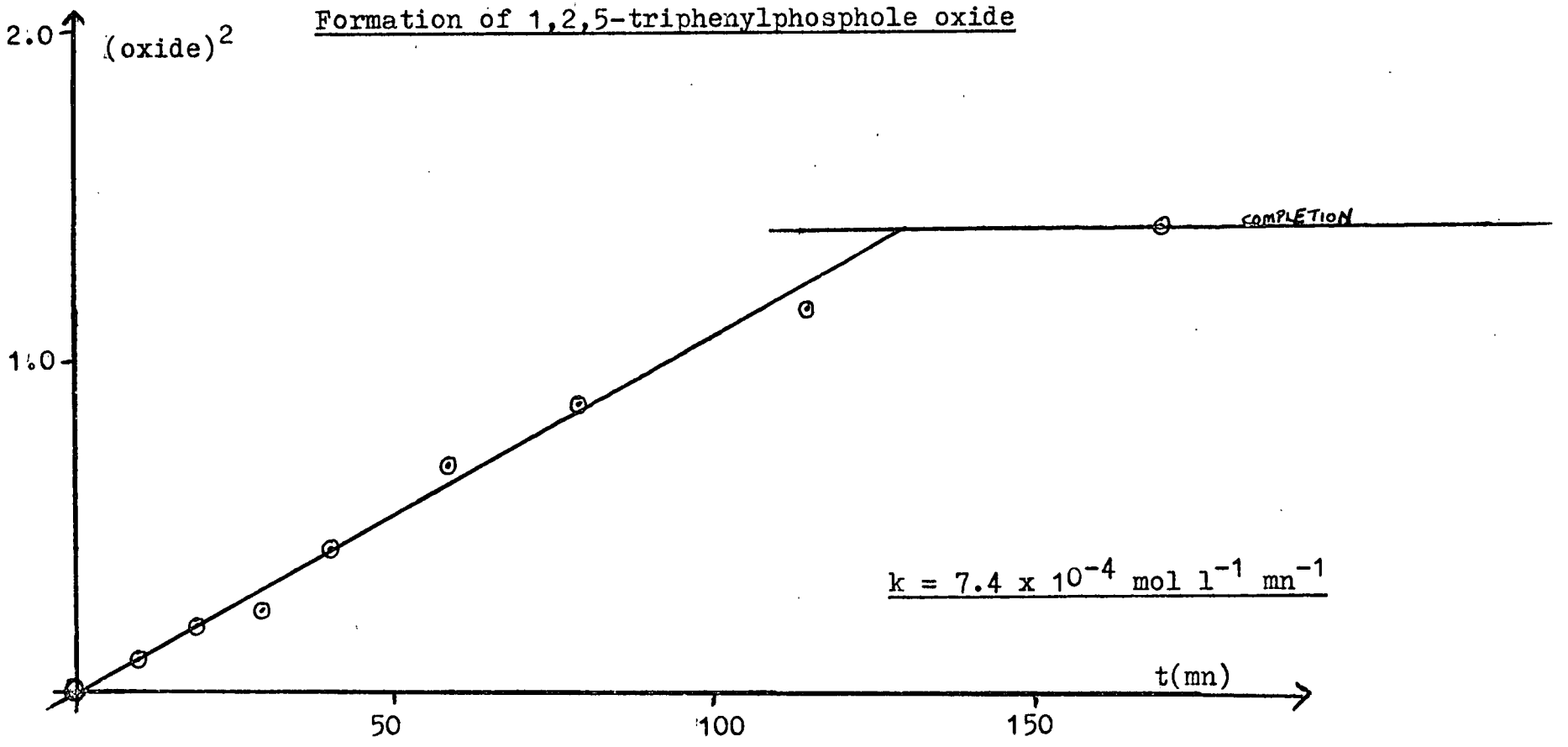
GRAPH 28 ^{31}P N.m.r. study

Formation of 1,2,5-triphenylphosphole oxide



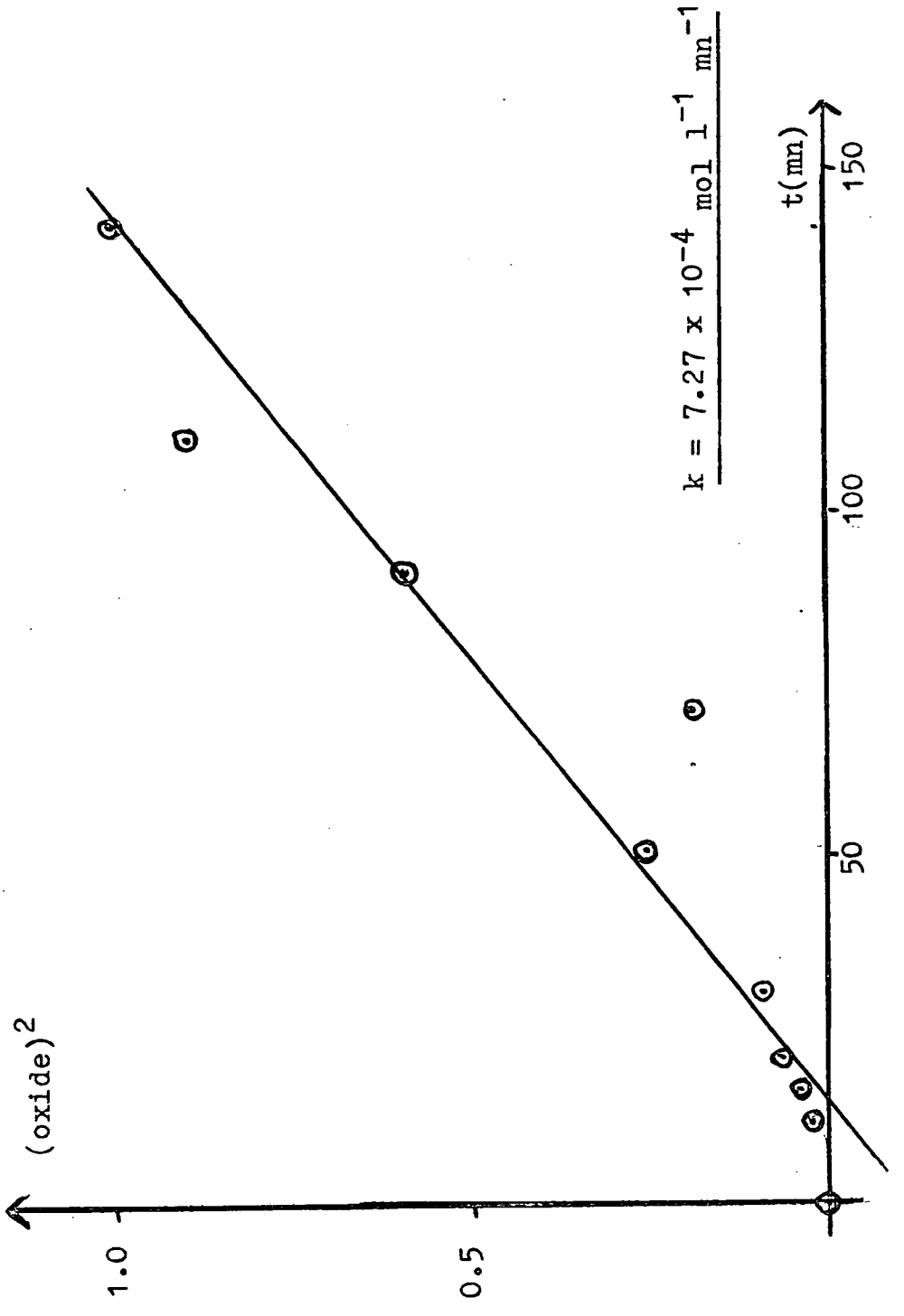
GRAPH 29 ^{31}P N.m.r. hydrolysis study

Formation of 1,2,5-triphenylphosphole oxide



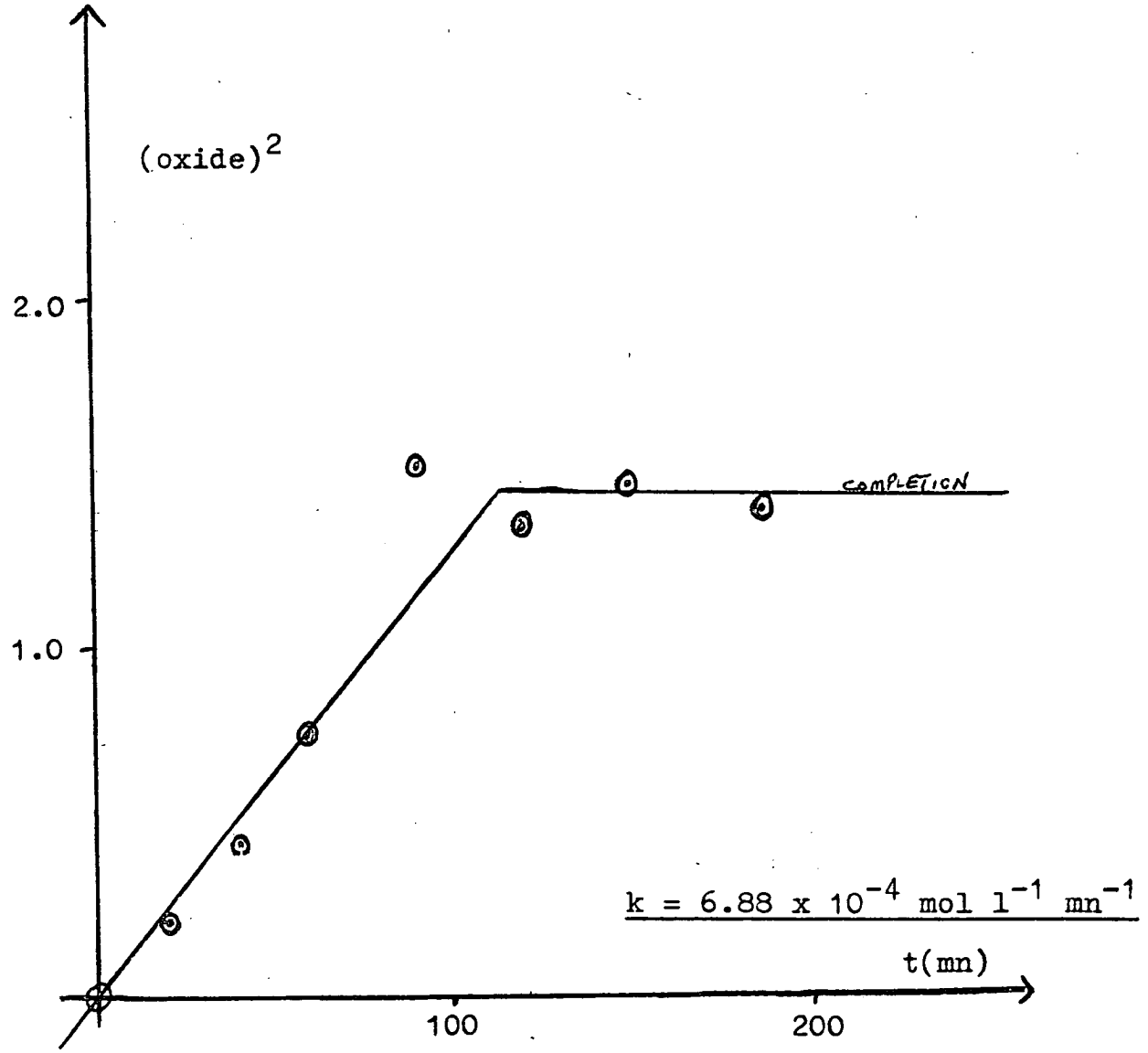
GRAPH 30 ^{31}P N.m.r. hydrolysis study

Formation of 1,2,5-triphenylphosphole oxide



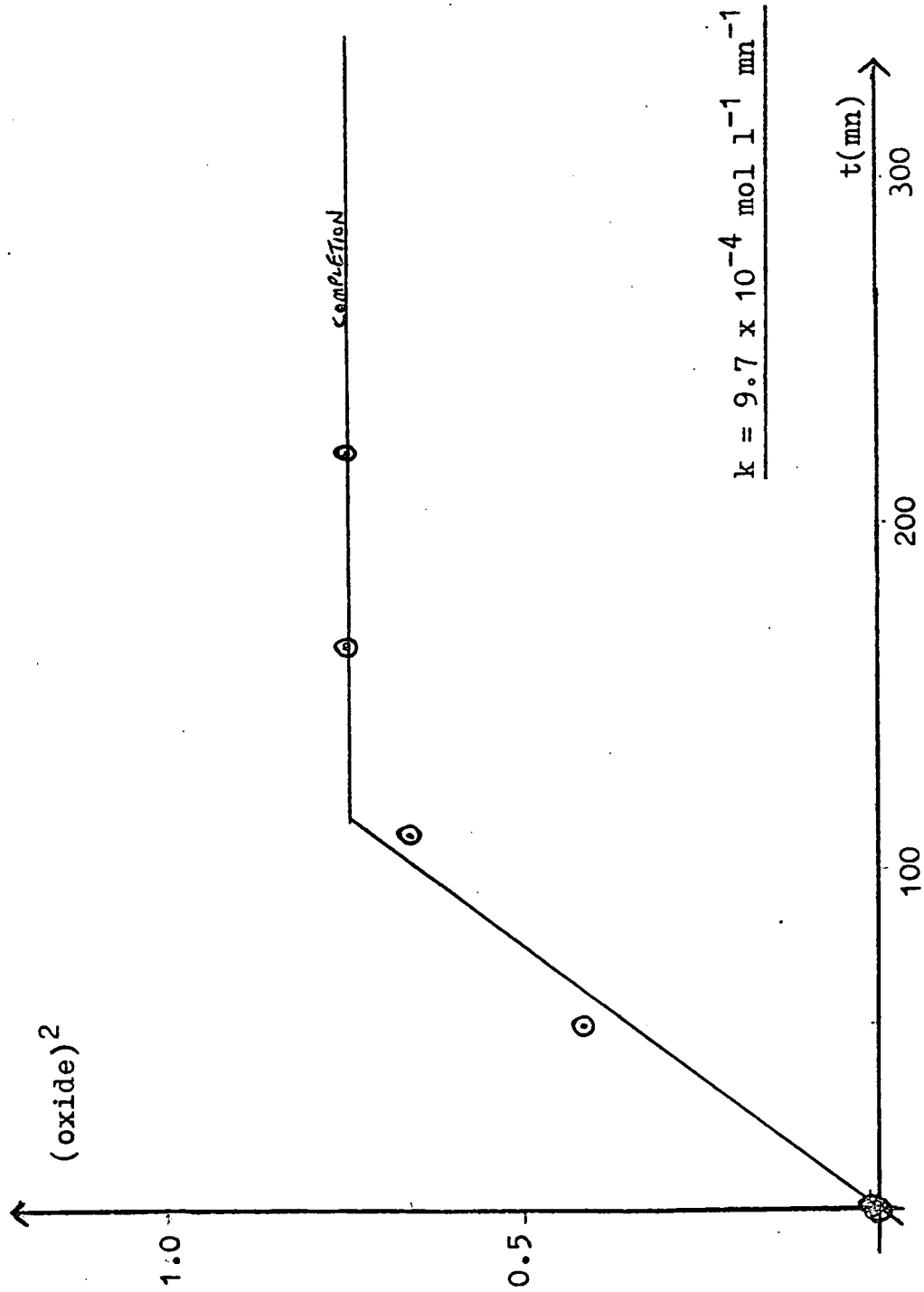
GRAPH 31 ^{31}P N.m.r. hydrolysis study

Formation of 2-phenyl-1,3,2-dioxaphospholan-2-oxide from N-(4-methyl-2-nitrophenyl)-imino-2-phenyl--1,3,2-dioxaphospholan



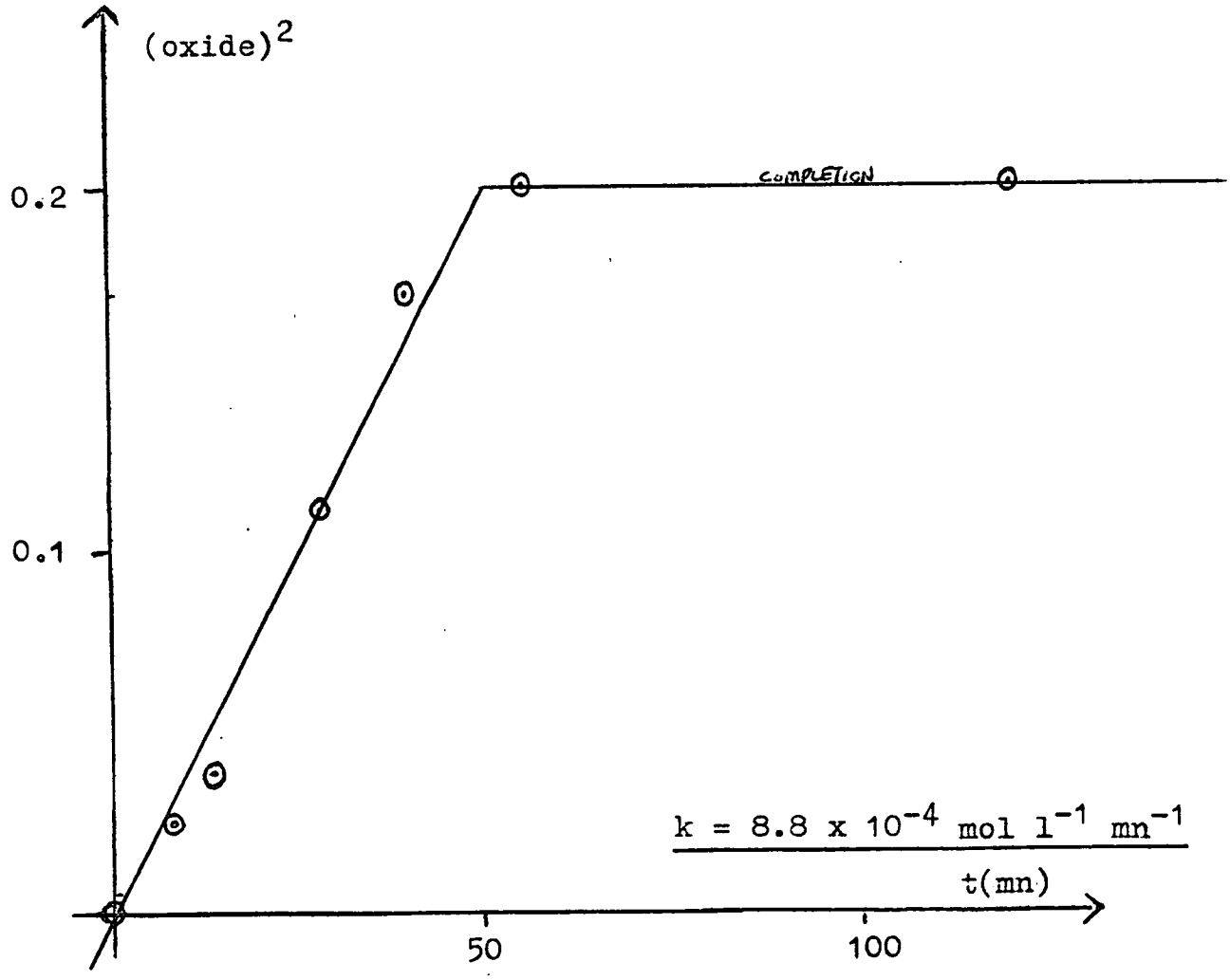
GRAPH 32 ^{31}P hydrolysis study

Formation of the oxide from N-(4-methyl-2-nitrophenyl)--imino-2-phenyl-1,3,2-dioxaphospholan



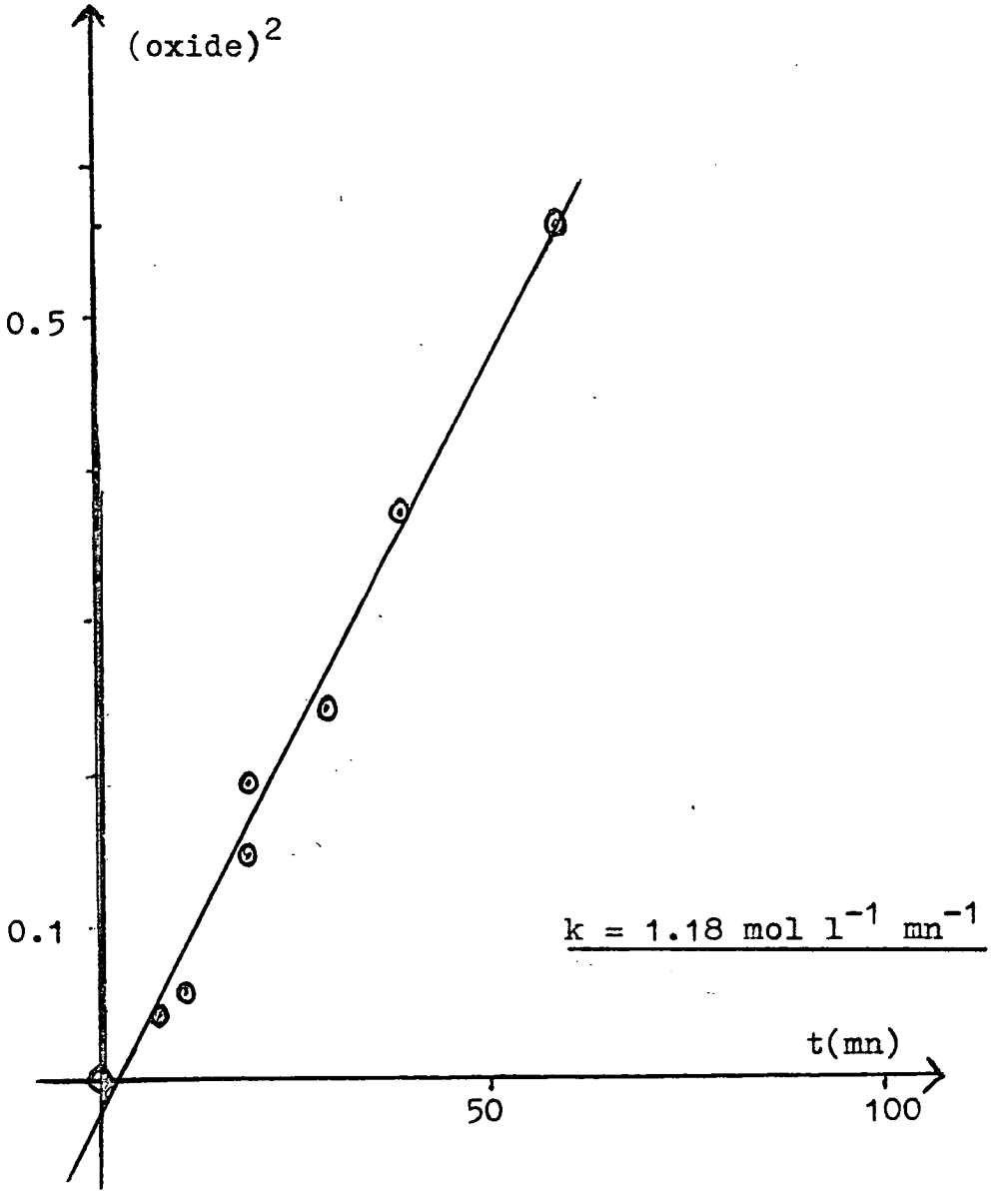
GRAPH 33 ^{31}P N.m.r. hydrolysis study

Formation of the oxide from N-(4-methyl-2-nitrophenyl)--imino—1-phenylphospholan



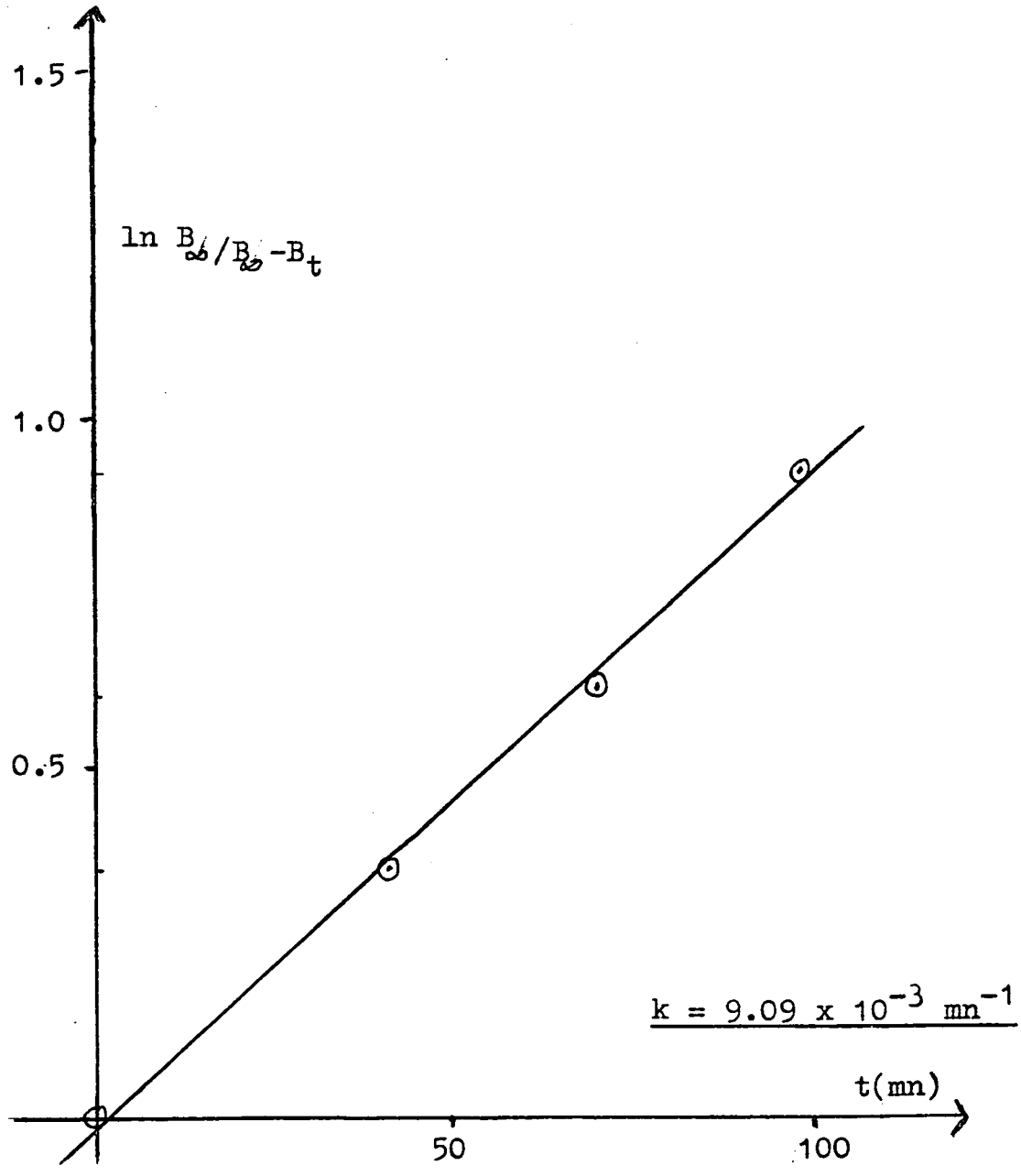
GRAPH 34 ^{31}P N.m.r. hydrolysis study

Formation of the oxide from N-(4-methyl-2-nitrophenyl)--imino-1-phenylphospholan

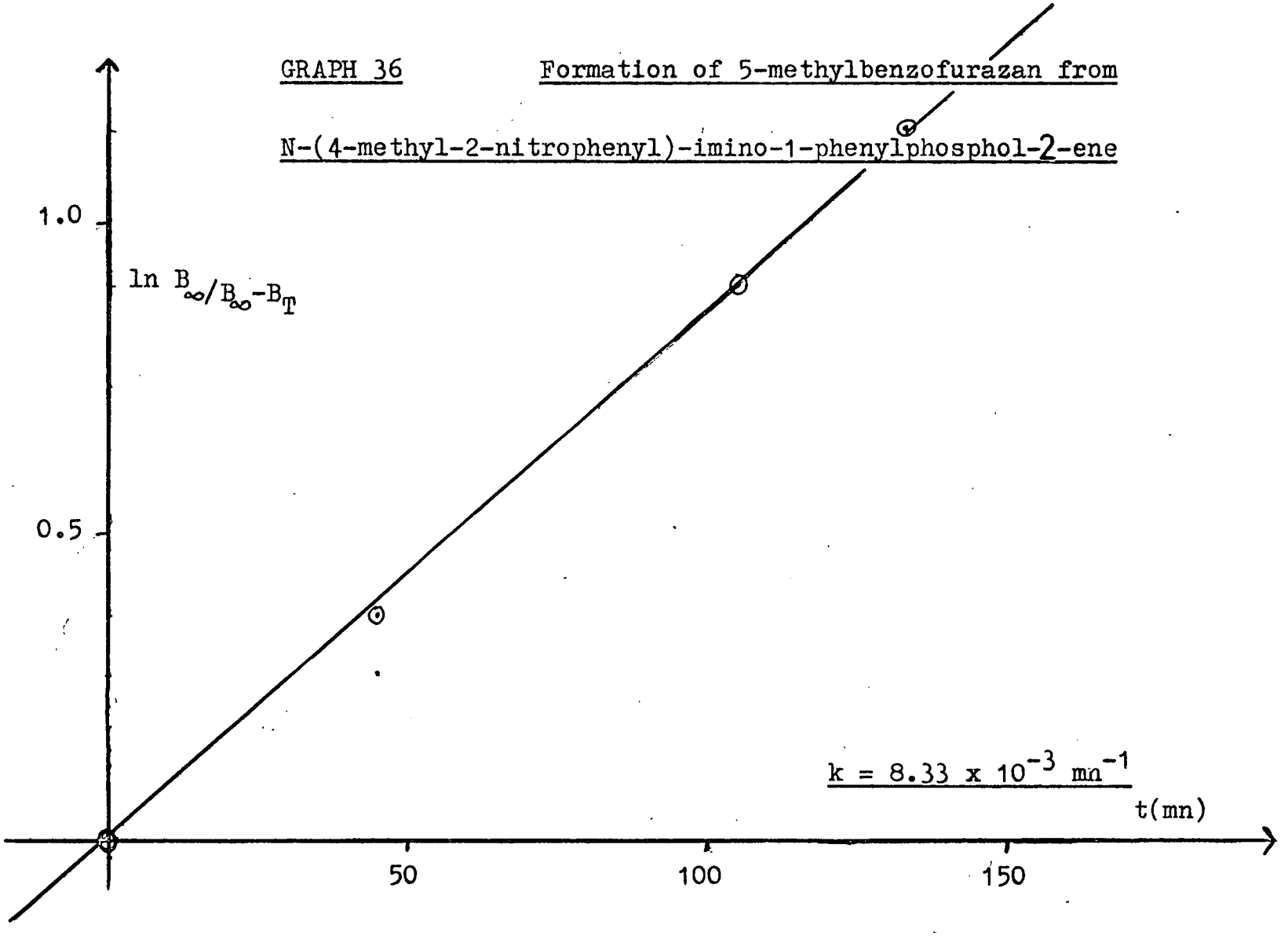


GRAPH 35 Formation of 5-methylbenzofurazan

N-(4-methyl-2-nitrophenyl)-imino-1-phenyl-phosphol-2-ene



GRAPH 36 Formation of 5-methylbenzofurazan from N-(4-methyl-2-nitrophenyl)-imino-1-phenylphosphol-2-ene



GRAPH 37

Decomposition in t-butylbenzene of
N-(4-methyl-2-nitrophenyl)-imino-1,2,5-triphenylphosphole.