SOME REACTIONS OF HYDROPEROXIDES IN THE PRESENCE OF CYCLIC PHOSPHATE ESTERS

by

Philip James Parsons

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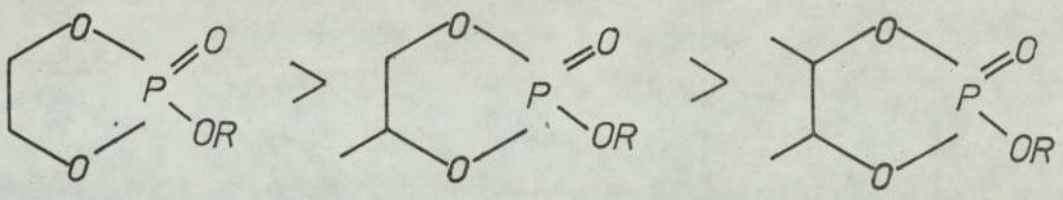
SUMMARY

A series of aromatic and aliphatic cyclic phosphate esters have been prepared. Certain of the aliphatic series were shown to react with hydroperoxides. The mechanism of the reaction was dependent on phosphate structure. Five membered aliphatic cyclic phosphates were found to react with hydroperoxides by an increasingly free radical mechanism as given by the following series.



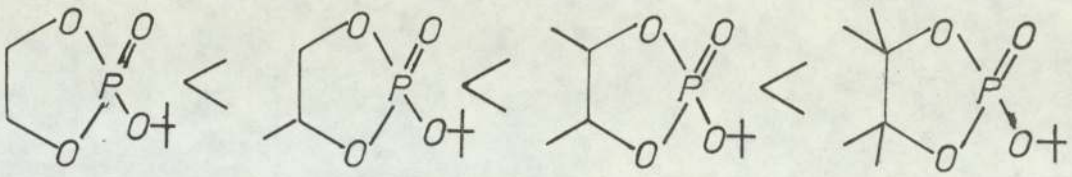
Ionic Free Radical

Six membered rings were shown to be inert to hydroperoxide.

In contrast to the aliphatic series, the aromatic five membered cyclic phosphates were found to be very active catalysts for the decomposition of hydroperoxides by an ionic mechanism. Relatively stable peroxides such as dicumyl and di-t-butyl peroxides were destroyed by the catechol phosphates, again by an ionic mechanism. Ring strain and pseudorotation were found to be important features of the catalytic activity, explaining why the decomposing effect was limited to five membered rings.

The t-butyl esters of five membered cyclic phosphates were found to be relatively unstable. The order of stability was shown to be in accordance with the inductive effect of ring substituents, thus

the following order of stability was found.



Pinacol cyclic phosphate was found to be the most stable, due to the four +I groups donating electron density to the phosphorus atom, leading to a less ionic transition state and hence a more stable system. The observation provided two useful results :

a) A convenient preparation of cyclic acid phosphates from the t-butyl esters.

b) Support for the free radical mechanism of hydroperoxide decomposition using +I substituted cyclic phosphates.

From these data it was possible to prepare other hydroperoxide decomposers, based on naphthalene and ethylene cyclic phosphates.

Metal complexes of catechol cyclic phosphate were prepared, and the effect on epoxidation and Baeyer Villiger reactions investigated. The vanadium and molybdenum chelates were powerful peroxide decomposers, and excellent catalysts for the epoxidation of olefins.

Finally photodegradation studies on polypropylene containing a novel naphthalene cyclic phosphite showed that this compound had effective antioxidant properties, and it was shown to decompose hydroperoxide more effectively than the corresponding catechol derivative.

The work described herein was carried out at the University of Aston in Birmingham between September 1974 and September 1975.

It has been done independently and submitted for no other degree.

P J Parsons.

October 1975

ACKNOWLEDGEMENTS

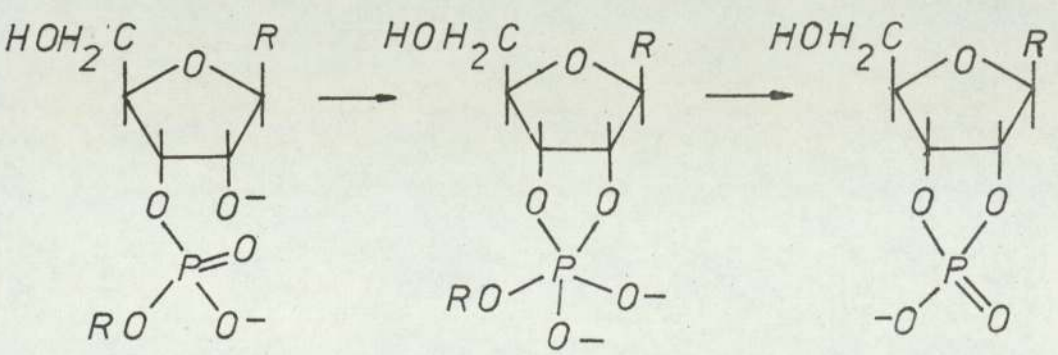
I would like to thank my supervisor Professor G. Scott, for all his help and endless encouragement during the past year. I wish to thank Mr. V. Laight and the Stores Department for their help in obtaining the necessary reagents for the project, and also my wife, Susan, for typing this thesis.

CONTENTS

1.0 INTRODUCTION

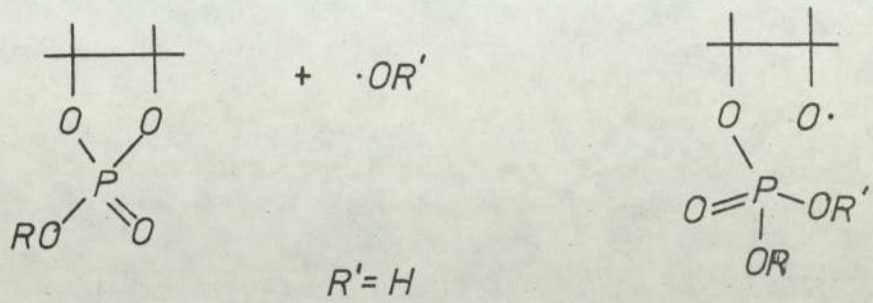
Cyclic esters of phosphoric acid have received intensive study over the years, partly due to their importance in biological functions. Fono[1] in 1947 noted the importance of neighbouring hydroxyl groups in causing the lability of diesters of phosphoric acid containing a glycol or glycerol residue; he postulated a cyclic triester intermediate in their hydrolysis, and also advanced the view that the lability of ribonucleic acid in alkaline media, in contrast to that of deoxyribonucleic acid, may be due to the cis hydroxyl group at carbon atom number 2 in the ribose residue of the former.

Brown and Todd[2] later suggested that nucleoside 2', 3' cyclic phosphates are intermediates in the hydrolysis of polynucleotides; such an intermediate was shown to exist[3] by isolation of a cyclic phosphate from the hydrolysates of ribonucleic acid using pancreatic ribonuclease. The formation of cyclic phosphates during the hydrolysis of nucleoside alkyl phosphates has been ascribed to reactions of the type (1)[4].



(1)

The irradiation of deoxyribonucleic acid in aqueous media has also been studied[35]. Viscosity changes compared with the effects of molecular oxygen, showed that scission of the intermediate cyclic phosphate bonds was caused by free radicals produced primarily from the solvent i.e.



It was shown that the yields of total peroxide[36] were always greater than that of hydrogen peroxide estimated by titanium complexing,[37] in irradiated D.N.A. solutions; this was explained by the presence of organic hydroperoxides. E.E. Hunter[38] examined the effects of phosphate on lipid peroxide formation when mitochondria are treated with oxidized and then reduced glutathione. The evidence suggested that phosphate inhibits G.S.H. and G.S.S.G. induced changes in mitochondria by a direct antioxidant route. Model systems for the hydrolytic action of ribonuclease on polyribonucleotides are provided by five membered cyclic phosphates.

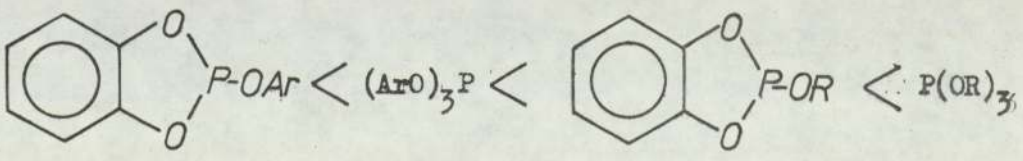
Certain fluorinated derivatives of phosphoric acid were shown to be active nerve poisons[5] and showed potential use as insecticides as well as in warfare.[6] [7] Despite the toxicity of many of these compounds, the use of organophosphites as stabilizers in polymer systems and

lubricants is well documented [8].

The mechanism of stabilization of polymer systems by phosphorus compounds was until recently, not well understood. Oxidation of hydrocarbons can be expressed as a chain series as follows (2):

$$RH + O_2 = \text{radicals} \quad (a)$$
$$R^{\bullet} + O_2 = RO_2^{\bullet} \quad (b) \qquad (2)$$
$$RO_2^{\bullet} + RH = RO_2H + R^{\bullet} \quad (c)$$

The role of an antioxidant in this case can be either to remove alkylperoxy radicals (b) or to remove hydroperoxide. It was considered that the hydroperoxide produced on ageing, underwent a stoichiometric reaction with the organophosphite, and this was responsible for the antioxidant action. Russian workers have published numerous papers [9] on the reaction of hydroperoxides with catechol phosphites, and the kinetics of the reaction were found to be first order with respect to both components, and correlation of structure with reactivity gave the following increasing order of rate.



i.e. Phosphorus is acting as a nucleophile and the order is in

agreement with the series established in the Arbuzov reaction[10].

Pobedimskii and Buchachenko studied the reaction of phosphites with hydroperoxide[9] by means of E.S.R.; following the decay of the 2,2',6,6'-tetramethylpiperidine-1-oxyl signal, these workers found the same kinetics by hydroperoxide analysis. An ion radical pair was postulated, which decayed to a radical pair; this could disproportionate or dissociate (3).

$$\begin{array}{l} RO_2H + (RO)_3P = \left[\dot{RO}_2H\ \overset{+}{P}(OR)_3\right] \\ \rightarrow \left[\dot{RO}\ \dot{P}(OH)(OR)_3\right] \\ \swarrow \qquad \searrow \\ ROH + OP(OR)_3 \qquad RO\cdot + \cdot POH(OR)_3 \end{array} \tag{3}$$

Denney and his coworkers[11] studied the reactions of cyclic phosphites with benzoyl peroxide, and concluded that phosphorus attacks the peroxidic oxygen, to give a phosphonium benzoate ion pair as an intermediate. Benzoate ion could then exchange or attack at carbonyl carbon to give products (4).

$$\begin{array}{l} R_3P + (C_6H_5CO_2)_2 \longrightarrow R_3\overset{+}{P}OCOC_6H_5 + \phi CO_2^- \\ \rightleftharpoons \qquad \searrow \\ R_3P(O_2CC_6H_5)_2 \qquad R_3PO + (C_6H_5CO)_2O \end{array} \tag{4}$$

Studies on the oxidation of five and six membered cyclic phosphites[39]

with dinitrogen tetroxide or ozone showed that the reaction was stereospecific and proceeds with retention of configuration about the phosphorus atom, suggesting that oxidation can occur via an ion pair intermediate or an SNi' mechanism.

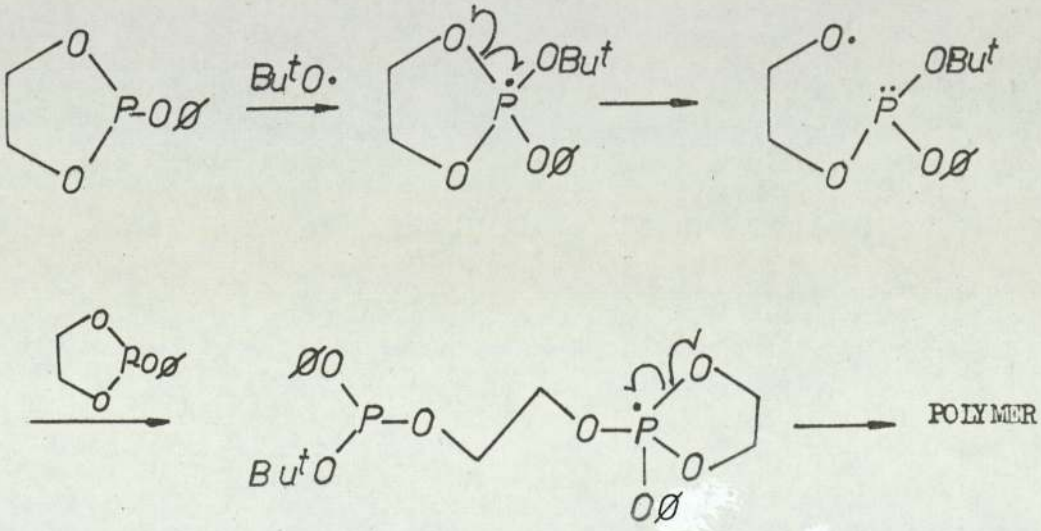
The autoxidation of tertiary phosphites was studied by Bentrude[12]. This work led to a further understanding of the fate of phosphoranyl radicals produced by phosphite / hydroperoxide reactions. It was found that t-butoxy radicals reacted with phosphites according to scheme (5).

$$Bu^tO\cdot + P(O\phi)_3 \longrightarrow Bu^tOP(O\phi)_2 + \phi O\cdot$$

$$Bu^tOP(O\phi)_2 \longrightarrow \text{(alkene)} + HPO(O\phi)_2 \qquad (5)$$

$$\phi O\cdot \xrightarrow{\text{H abstraction}} \phi OH$$

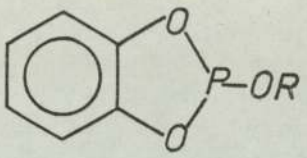
When 2-phenoxy-1,3,2-dioxaphospholane was similarly treated, polymeric material was obtained. The mechanism postulated involved free radical scission of the dioxaphospholane ring (6).



(6)

This work gave similar results to those obtained by Griffin and Plumb[13] who reported facile oxidation of a variety of alkyl phosphites to the corresponding phosphates in very high yields, but only partial oxidation of triphenylphosphite in the corresponding reaction time.

Recent work at Aston[14][15][16] has shown that for compounds of type 1



1

(2-alkoxy-4,5-benzo-1,3,2-dioxaphospholane)

The antioxidant activity is not entirely due to 1, but a catalytic species derived from 1.

The reaction of 1 with cumene hydroperoxide (C.H.P.) eventually leads to a pseudo first order hydroperoxide decomposition, identical to that observed with the corresponding phosphate (Fig.1).

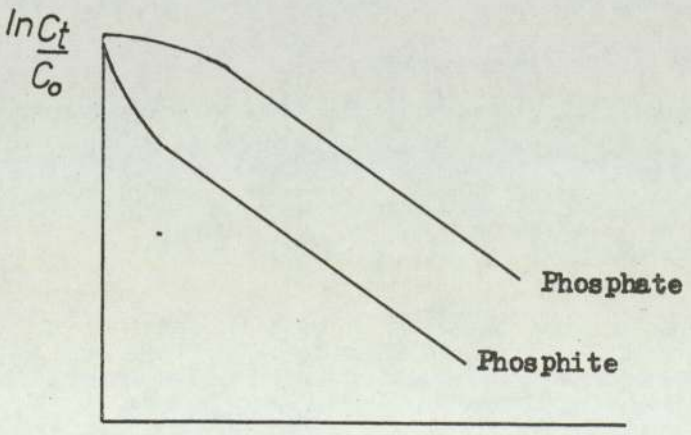
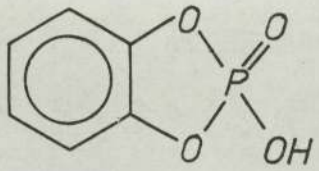
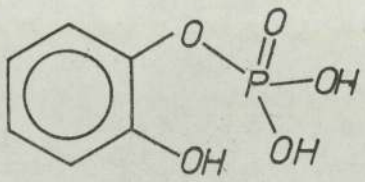


Fig.1

Products isolated from the reaction between C.H.P. and 2-(4-methyl-2,6-di-t-butylphenoxy)-4,5-benzo-1,3,2-dioxaphospholane were also shown to be powerful catalysts for the decomposition of hydroperoxide, namely 2-hydroxy-2-oxo-4,5-benzo-1,3,2-dioxaphospholane 11, and its hydrolysis product 11a.



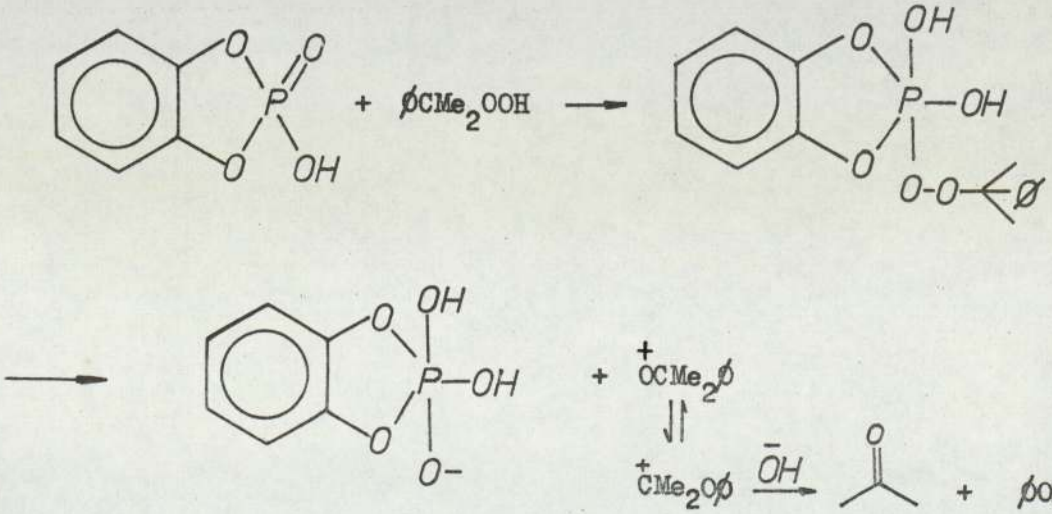
II



IIa

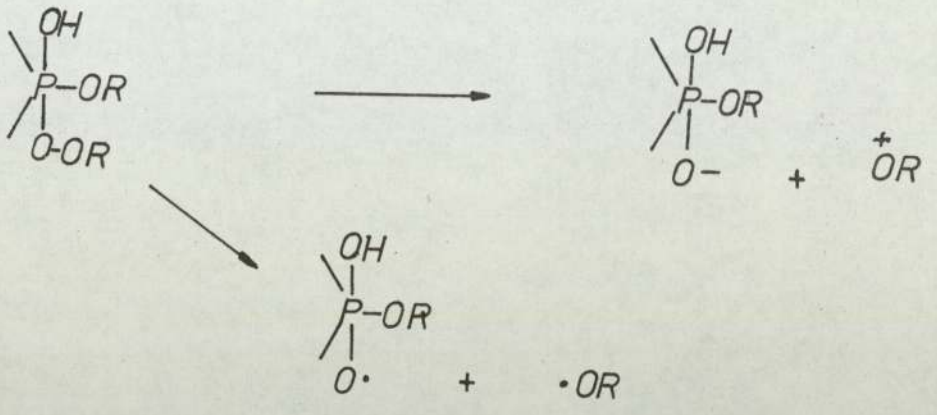
The hydroperoxide decomposition products were those expected from a typical Lewis acid catalysed reaction giving mainly phenol and acetone by an ionic mechanism[16], involving a pentacoordinate phosphorus intermediate, similar to that postulated by Brown and Todd in the hydrolysis of ribonucleic acid[2].

Scheme (7) shows the decomposition of C.H.P. using catechol cyclic phosphate.



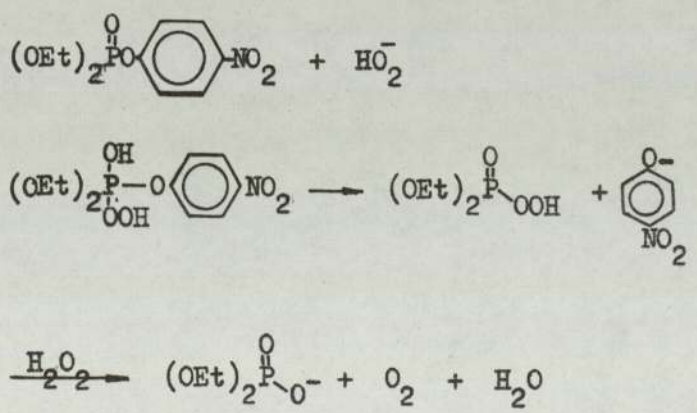
(7)

Some α-methyl styrene was noted in the reaction mixture, and was explained by homolysis of the peroxy bond in the transition state; in a similar manner to that described by Pobedimskii[9] (8).



(8)

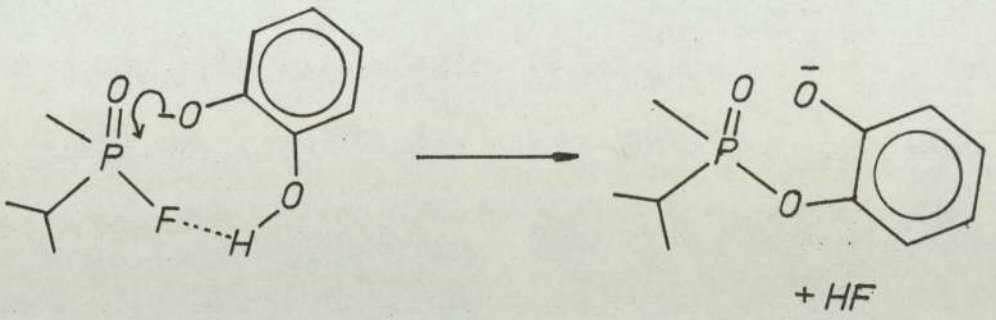
The enhanced rate of hydrolysis of paroxon (p-nitrophenyl diethyl-phosphate), in the presence of hydrogen peroxide was noted by Epstein et al.[17]. A mechanism was formulated, by analogy to the reaction of hydrogen peroxide with isopropyl methylphosphonofluoridate[18]. (9



(9)

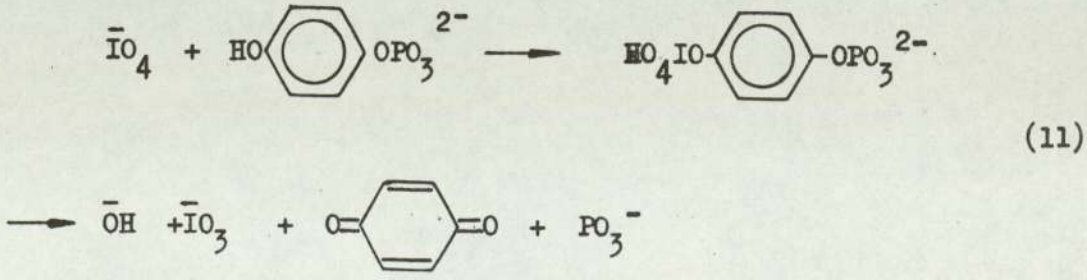
The reaction was found to be first order with respect to hydroperoxy anion and substrate. Although perhydroxyl ion is less basic than hydroxyl[19] its reaction rate with peroxon was found to be one hundred times faster than hydroxyl ion.

The interatomic distances between the hydrogen and charged perhydroxyl oxygen were found to be sufficiently close to allow the operation of a push pull type of mechanism similar to that observed for the reaction of catecholate ions with methylisopropylphosphonofluoridate[20] (10).



(10)

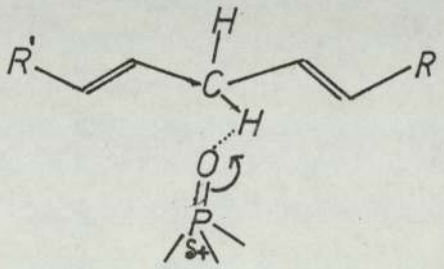
Models for oxidative phosphorylation have been discovered[21][22]. 1,4-Naphthoquinone monophosphate is stable in alcohols when air is excluded. If iodine is added, or air admitted, oxidation occurs with the formation of the monoalkyl ester of phosphoric acid. Enzymic oxidation of 1,2-propanediol phosphate to acetol phosphate and reversible oxidation was shown with rabbit muscle enzyme by Huff et al.[23]. Brooks et al. have shown as part of a study on the oxidation of quinol phosphates that periodic acid reacts with p-hydroxyphenylphosphate. Phosphorus-oxygen fission was noted at pH 6 and was explained by the following mechanism (11).



(11)

The monoanion-dianion reaction appeared to involve metaphosphate elimination in a slow step as shown by Todd et al.[25].

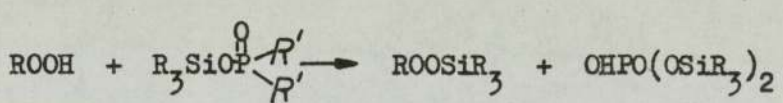
The importance of phosphate esters in polymer systems has been the subject of many patent specifications. Eastmann Kodak[26] found that aryl amine phosphates were useful lubricant antioxidants. Ukrami et al.[27] found that glyceryl phosphates were useful antioxidants in oils. It was later shown that phosphoryl choline and phosphorylethanolamine gave antioxidant activity in unsaturated fatty acids[28]. The infra-red spectrum of methyl linoleate containing 0.03% phosphoryl choline showed the same characteristic absorption bands as those observed in the case of β -glyceryl phosphoric acid and tributyl phosphate to the same substrate. These results suggested that the mechanism for the antioxidant action of phosphoryl choline involves interaction of the phosphoryl group with the α methylene group of the methyl linoleate. i.e.



Since the results of alcoholysis of lecithins indicated that the glyceryl moiety in organic solvents is in the trans-trans conformation, the phosphoryl choline is thus sterically hindered by an α acyl group in such a way that the phosphoryl group cannot

interact with the substrate molecule, thus explaining the ineffectiveness of lecithins as antioxidants in liquid substrates. Work in this laboratory however, (see chapter 4) has shown that aliphatic cyclic phosphates react with hydroperoxides; in the case of glyceryl - phosphoric acid the cyclic ester formed by dehydration may have more effect on antioxidant activity than interaction of phosphoryl groups with α methylene groups in the linoleate ester.

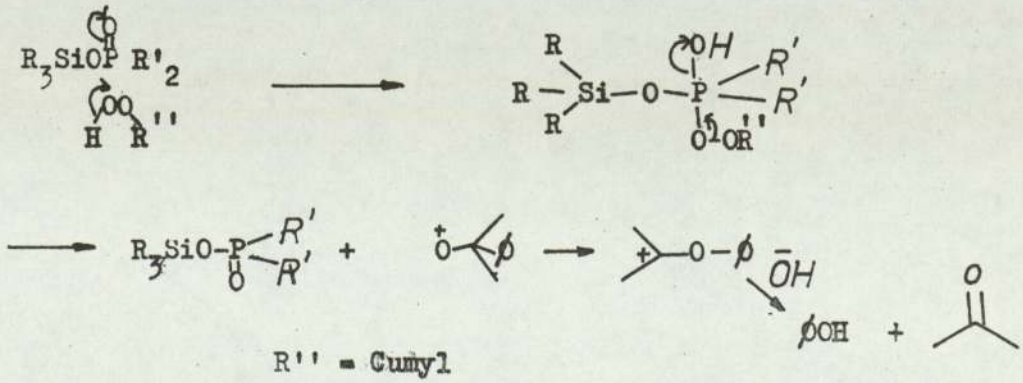
Silyl phosphates were found to be effective oxidation inhibiters in hydrocarbon systems;[30] it was shown that the triorganosilyl phosphates were peroxide decomposers, and a reaction mechanism was postulated to account for the initial induction period, and the formation of phenol (12).



$$ROOH + R_3SiOP(O)(R')_2 \longrightarrow ROOSiR_3 + OHPO(OSiR_3)_2 \qquad (12)$$

$$R' = R_3SiO$$

i.e. formation of a peroxysilane followed by a phosphoric acid catalysed cleavage. Another possibility is the formation of a pentacoordinate complex, which could then decompose to give ionic hydroperoxide decomposition products (13).



(13)

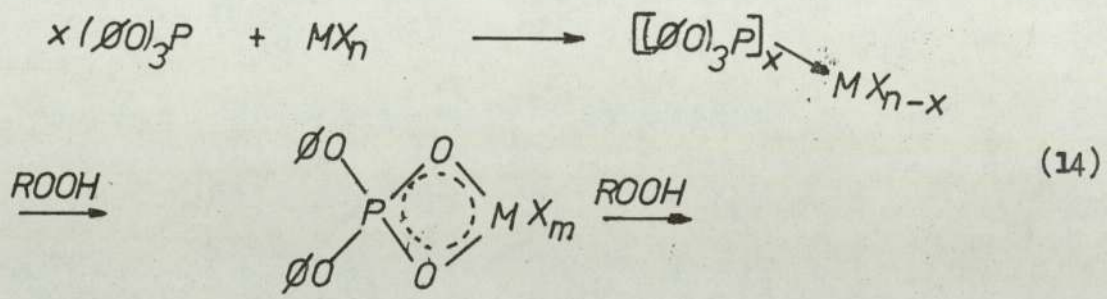
R'' = Cumyl

In the previous case the silyl phosphate would act as a catalyst for the decomposition of cumene hydroperoxide. It was shown that with increasing numbers of silyl groups antioxidant activity increased. Enhancement of peroxide decomposition was also noted when a phenyl group was present; this is in agreement with the present study.

A.G. Popev et al. found that 2,6-diisobornyl-4-methylphenyl-catechol phosphate was a stabilizer in polypropylene systems[31]. 2-(3-Hydroxy-4-benzoylphenoxy)-4-methyl-1,3,2-dioxaphosphorinane-2-oxide was found to be a useful antioxidant in polypropylene[32]. This material gave an embrittlement time of 775 hr. compared with 333 hr. for a preparation containing $HO(C_8H_{17}O)C_6H_3Bz$. Although antioxidant activity was observed in the last two cases, no attempt appears to have been made to rationalize the experimental data, and produce mechanisms for this phenomenon.

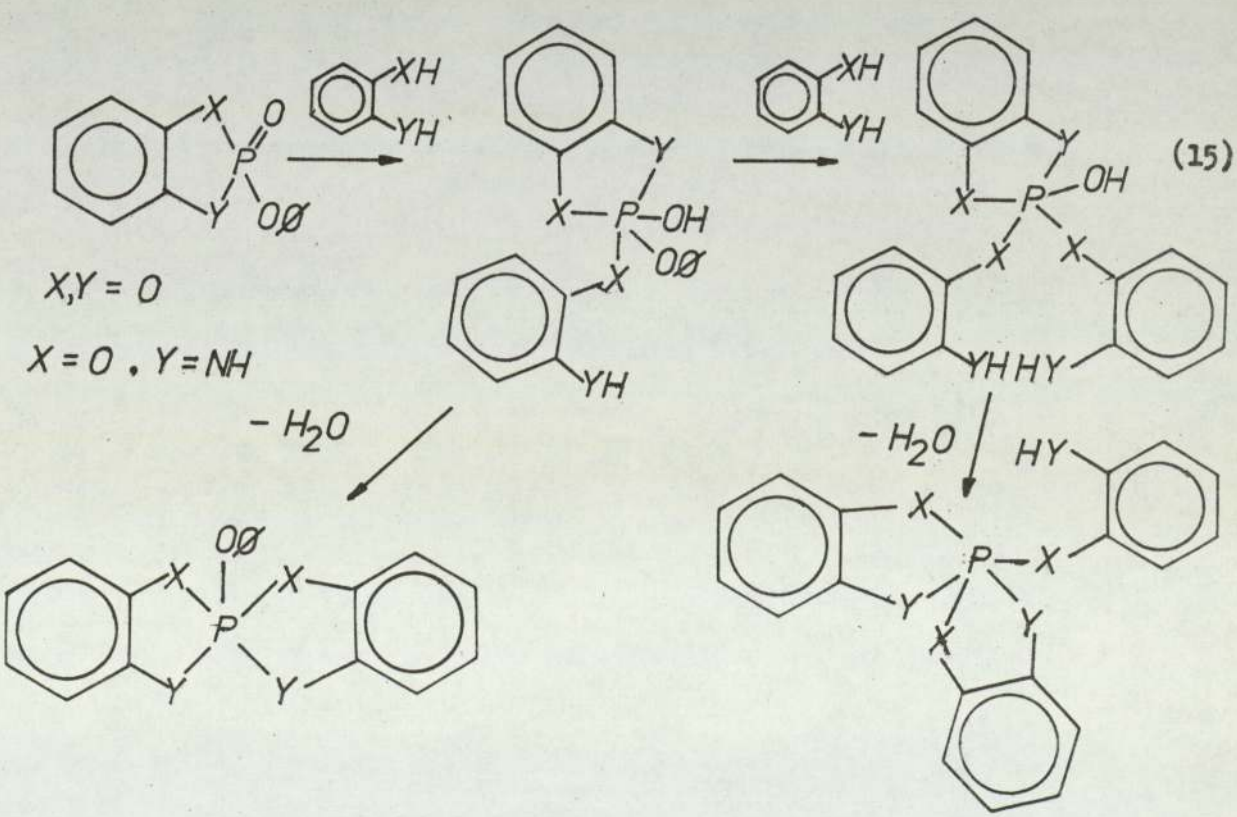
In a recent paper by Pobedimskii[33] a description was given of a catalytic peroxide-decomposing effect observed with triphenyl-phosphite in the presence of metal ions. This may well be due to the formation of a metal chelate which may effect the phosphorus-oxygen $d\pi - p\pi$ bonding sufficiently to cause a reaction with hydroperoxide. (See 14). The increased reactivity of five membered cyclic phosphates toward hydrolysis over six membered cyclic phosphates led to the conjecture that variations in $d\pi - p\pi$ bonding might be responsible

for the major part of the kinetic acceleration[40]. This was supported by Brown and Todd who determined the ^{31}Phosphorus n.m.r. spectra of various five membered cyclic phosphates, and found less electron shielding of the phosphorus nucleus which is consistent with diminution of $d\pi$-$p\pi$ double bond character.[41]



(14)

Evidence for the formation of pentacoordinate intermediates in displacement reactions involving catechol phosphates was presented by Koizumi et al.[34]. 2-Oxo-2-phenoxy-4,5-benzo-1,3,2-dioxaphospholane was treated with o-hydroxyaniline, and later catechol. All the intermediates in the reaction were isolated as follows (15).



(15)

Westheimer first proposed the pseudorotation mechanism in the hydrolysis of five membered cyclic phosphates,[88] and hence the formation of pentavalent intermediates. The latter work by Koizumi supports the pseudorotation mechanisms, and the formation of pentavalent intermediates in the hydroperoxide / phosphate reactions.

1.1 Scope and object of the project.

The chemistry of hydroperoxides, although an extensive field, still remains a relatively new area for research; this is probably due to the reported toxic and explosive nature of many of these compounds (even though they can be handled safely, and in some cases distilled or sublimed).

The present work is concerned with the reactions of cyclic phosphate esters with various aralkyl hydroperoxides and peroxides, in order to ivestigate the reason why certain cyclic phosphates are efficient catalysts for the decomposition of hydroperoxides, despite reports of the low reactivity of cyclic phosphites towards hydroperoxide (43).

The study involves detailed consideration of the effects of ring strain, conformation, structure inductive effects, $d\pi - p\pi$ bonding, extended conjugation and steric hindrance on reactivity in order to produce (with relevant kinetic data) mechanisms to explain the observed reactions and products. From thesedata it may then be possible to design an efficient peroxide decomposer for use as an antioxidant in polymer systems, and also to develop new compounds that may catalyse epoxidation and Baeyer Villiger reactions to produce compounds of commercial importance.

It is hoped that the contents of this thesis will contribute to the knowledge that exists on the chemistry of inhibition of organic oxidation processes, and also to the methods of synthesis of organic cyclic phosphates.

2.0 EXPERIMENTAL SECTION

2.1 Instrumental Techniques - Spectra.

Infra red spectra were recorded on a Perkin Elmer 225 for measurement of absorptions lower than 600 cm^{-1}.

Ultra violet spectra were recorded on a Perkin Elmer 137.

Mass spectra were recorded on an A.E.I. MS9 double focussing spectrometer with 70 eV acceleration. G.L.C. mass spectra were recorded using the same instrument, but with a Pye 104 series chromatogram facility.

Nuclear Magnetic Resonance spectra were run on various instruments ; the Perkin Elmer R10 and R12 were used for 60 MHz work. Tetramethyl silane was used as a reference for work in organic solvents.

^{31}P spectra were recorded relative to 85% orthophosphoric acid.

2.2 Analysis.

2.2.1 Gas Chromatography.

A Pye series 104 gas chromatograph was used for all samples. A flame ionization detector was used, and five foot all glass columns filled with polyethyleneglycol adipate (10% on celite) were used for phenolic samples . After preparation the columns were aged for 30 hours at 180 °C. All service gases were purified by passage through freshly activated molecular sieves (UC type 13X) and nitrogen was

used as the carrier gas. Internal standards were used for quantitative G.L.C., as errors could arise in measuring small volumes. In most cases p-cresol or dibenzyl were found to be reliable internal standards, and plots of $\frac{\text{peak area of product}}{\text{peak area of standard}}$ versus concentration gave good straight lines. The most convenient method for quantitative work was found to be a temperature programme from 85 - 180°C at a 4°/ minute heating rate ; which gave an excellent separation of the peaks and a straight base line. The average of two injections was taken, and the spectrum on the injection point was replaced after every 10 - 20 injections. Table 1 shows the retention distances for various reaction products and internal standards.

TABLE 1

PRODUCT	RETENTION Isothermal	DISTANCE cm Programme	INTN STD.	PROGRAMME °C
Acetone	2.2	2.3	p - cresol	85 - 180
Cyclohexene	4.0	4.5	"	"
Cyclohexene Epoxide	-	10.8	"	"
∝-Methyl Styrene	-	16.0	"	"
Cumyl Alcohol	11.5	47.5	"	"
Cyclohexanone	-	5.0	"	"
Phenol	18.0	58.0	"	"
Acetophenone	10,0	40.5	"	"
∝-Phenyl Ethanol	-	36.5	"	"
Acetaldehyde	-	1.5	"	"
Caprolactone	22.8	-	"	"
Chlorobenzene	-	10.5	"	"
Benzene	4.0	-	"	"

Isothermal = 180°C

2.2.2 Thin Layer Chromatography. (T.L.C.)

T.L.C. was used to identify a variety of phosphorus, and hydroperoxide decomposition products. Silica Gel plates (E. Merck) were used for many components and the following table shows suitable solvents and developing agents for a variety of products. (Table 11).

TABLE 11

SUBSTANCE	SOLVENT	DEVELOPING AGENT
Pinacol cyclic phosphate	ØH / EtOAc 9:4	I_2 vapour
Cumene hydroperoxide	ØH / EtOAc / HOAc 100/1/0.1	KI (aqueous)
Dicumyl peroxide	CCl_4	$SbCl_5$ / CH_2Cl_2
Phenol	ØH / EtOAc 100/1	$FeCl_3$ (aqueous)
Hydroxyphenylphosphate	Butanol / acetic acid	$FeCl_3$ (aqueous)

Paper chromatography was used to separate catechol hydroxy phosphate esters, ferric chloride was found to be a suitable developing agent, and butanol : acetic 100 : 1 a suitable solvent.

2.2.3 Elemental Analysis.

Elemental analysis was performed on a standard Perkin Elmer analyser. Phosphorus analysis was performed in the laboratory by a modification of the method of Vogel[44] for the analysis of phosphate in rock. The method is based on the precipitation of quinoline phosphomolybdate, which is isolated and titrated with standard alkali.

$$(C_9H_7N)_3H_3PO_4 12MoO_3 + 26NaOH \rightarrow$$

$$Na_2HPO_4 + 12Na_2MoO_4 + 3C_9H_7N + 14H_2O$$

The method is rapid and has the following advantages :

(1) Quinoline phosphomolybdate is very insoluble in water.

(2) Quinoline is a weak base and does not interfere in the titration.

A sample of the cyclic phosphate (0.2g.) was hydrolysed in boiling aqueous perchloris acid (10ml.) containing water (20ml.) The resulting solution was cooled and hydrochloric acid (20ml. 0.1m.) added. The solution was then made up to 100ml. with distilled water. An aliquot of the phosphate solution (10ml.) was transferred to a conical flask. Concentrated hydrochloric acid (30ml.) was added, followed by sodium molybdate solution (15% aqueous, 30ml.). The solution was refluxed for 1 min., and quinoline hydrochloride solution (60ml. 10%) added dropwise. A crystalline precipitate formed, and was filtered and washed. The precipitate was transferred to the original conical flask plus 30ml. water and standard alkali (50ml. 0.5m.). The solution was heated until all the precipitate had dissolved, and was back titrated with hydrochloric acid (0.5m.) using phenolphthalein / thymol blue as indicator.

1ml. 0.5N NaOH $\equiv$ 1.366mg. P_2O_5 $\equiv$ 0.5964mg. P

2.3.0 Kinetic Studies .

The kinetics of the decomposition of the t-butyl esters of phosphoric acid were followed by a simple technique, Fig.11, following the evolution of isobutene by measuring the velocity of a mercury bead through a piece of glass capillary tubing of uniform bore. Knowing the diameter of the tubing and the length and weight of the mercury bead, it was possible to calculate the volume, and hence the weight, of isobutene given off per unit time. The kinetics of hydrolysis of the aliphatic cyclic phosphates were followed by an n.m.r. technique; the collapse of one of the methylene signals with time was followed, and the area under this peak was related to the concentration of cyclic phosphate.

The kinetics of epoxidation were followed by quantitative G.L.C.; samples of the reaction mixture were taken at set time intervals and injected on to a G.L.C. column, the amount of epoxide formed after the set time intervals was thence calculated.

The kinetics of hydroperoxide decomposition was followed by an n.m.r. technique. A resonance peak (usually acetone) was selected, and the rate of appearance of the decomposition product noted; to compare this, the kinetics of the decomposition of various hydroperoxides were followed by an iodometric technique[45]. Many methods exist for the estimation of hydroperoxide e.g. the arsenious oxide method[46]; however this method takes approximately twenty

minutes for each sample and is useless for following reasonably fast reactions. The simplest and most precise method for the estimation of hydroperoxide in the present study was found to be a modification[47] of the technique using isopropanol-sodium iodide mixtures[45]. The advantages of this method are :

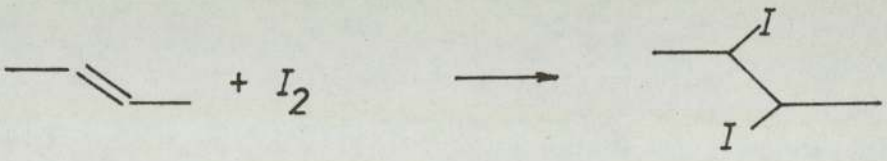
(1) Rapid and reproducable.

(2) Loss of iodine by boiling is prevented since the following equilibrium exists :

$$I_2 + I^- \longrightarrow I_3^-$$

sodium iodide is more soluble in isopropanol than potassium iodide so that the equilibrium is always to the right and I_3^- is non volatile.

(3) Triiodide ion does not react with any hydroperoxide decomposition products, and so errors are eliminated due to the following reactions which are possible with iodine.



(4) No reaction is observed with cyclic phosphates, which would lead to errors due to the catalyst concentration.

(5) The use of non aqueous solvents prevents low results, as the peroxide-iodide reaction is retarded in aqueous media

The reagents used in the hydroperoxide analysis were as follows :-

Sodium iodide 10% in isopropanol (Solution 1)

Acetic acid 10% in isopropanol (Solution 2)

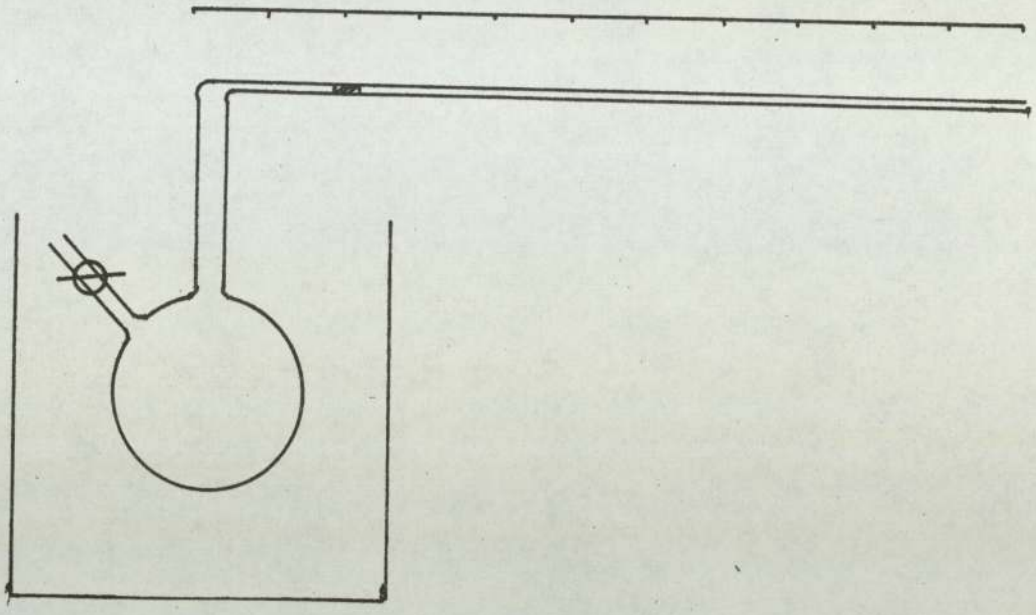
Sodium thiosulphate solution was prepared [44], and standardized using potassium bromate [44]. Solution 1 (20ml.) and Solution 2 (10ml.) were mixed in a conical flask. The reaction mixture (0.2ml.) was added and the solution refluxed for five minutes. The solution was diluted with distilled water, and the liberated iodine (as I_3^-), titrated with standard sodium thiosulphate solution (0.0103m.). The blank titration performed during each experiment was small.

The kinetic experiments were performed using a three necked flask fitted with a drying tube, nitrogen inlet, stirrer, and a device for admitting the catalyst. (Fig.III). Usually the hydroperoxide solution (10ml. of required concentration) was allowed to reach the required temperature in an oil bath; the catalyst was then added and the reaction followed after set time intervals.

2.3.1 Kinetic Experiments.

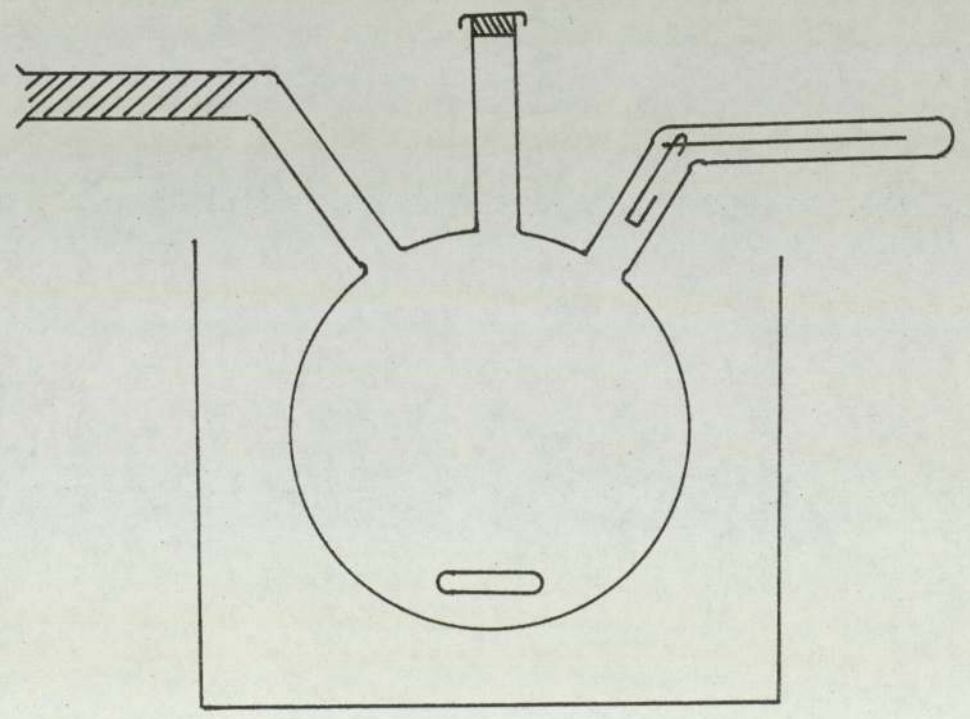
Kinetic experiments were performed in an insulated bath filled with Shell Risella Oil for use at 65-80°C with a temperature

Fig. II



Apparatus for following the evolution of isobutene.

Fig. III



Apparatus for following the decomposition of hydroperoxide.

control of ± 0.05°C. For temperatures above 80°C silicone oil was used. For experiments involving ethylbenzene hydroperoxide, small sealed glass vessels were used to prevent loss of acetaldehyde by evaporation.

2.4. Purification of solvents and reagents.

Boiling points are taken from standard texts[48][49] unless stated.

Acetone was purified by shaking with a small quantity of potassium permanganate, followed by agitation with anhydrous calcium sulphate. After filtration the product was distilled. B.pt. 56-7°C.(Lit. 56.2°, 760.)

Acetophenone was distilled under nitrogen B.pt. 199-201°C.(202°, 760.)

Benzene was dried over sodium and distilled under nitrogen B.pt. 80°C. (80.1°, 760.)

Chlorobenzene was refluxed over phosphorus pentoxide and distilled thrice using a two foot Vigreux column. B.pt. 131°C. (132°, 760.)

Cumene was refluxed over metallic sodium in a nitrogen atmosphere, and distilled twice through a two foot Vigreux column. B.pt. 152°C. (152- 3°, 760.)

Cumene hydroperoxide was purified via the sodium salt[50] followed by liberation of the hydroperoxide by solid carbon dioxide . The purified material was distilled under reduced pressure in an atmosphere of nitrogen.B.pt.50°C, 0.01mm Hg. (51°,0.01.[50])

t-Butyl hydroperoxide was purified in a similar manner to cumene hydroperoxide. B.pt. 40°C./ 19mm Hg. (35°, 20.)

Diethyl ether was dried and distilled over sodium. B.pt. 34°C. (34.6°, 760.)

Cyclohexanone was distilled before use. B.pt. 156°C. (155.6°, 760.)

Ethylene glycol was distilled under nitrogen followed by storage over anhydrous sodium sulphate, redistillation gave a viscous liquid. B.pt. 198°C. (197.6°, 760.)

Methanol was purified by the magnesium iodine method[48] followed by distillation under nitrogen. B.pt. 63°C. (64.7°, 760.)

Phenol was redistilled . B.pt. 180°C. (182°, 760.)

Catechol was redistilled before use. B.pt. 246°C. (245°, 760.)

Phosphorus trichloride was redistilled. B.pt. 76°C. (75-7°, 760.)

Phosphoryl chloride was distilled before use. B.pt. 107°C. (107°, 760.)

Tetrahydrofuran was purified by refluxing over lithium aluminium hydride followed by distillation under nitrogen. B.pt.65°C. (66°, 760.)

Nitrobenzene was purified by refluxing over phosphorus pentoxide followed by distillation through a two foot lagged Vigreux column. B.pt. 212°C. (210-2°, 760.)

p-Cresol was distilled under nitrogen. Bpt. 198°C. (201°, 760.)

Cumyl alcohol (2-phenylpropan-2-ol) was distilled at 92°C./14mm Hg. followed by recrystallization from petroleum ether (30-40°) m.pt. 34°C. (36°).

<u>α-Methyl styrene</u> (2-phenylpropene) was distilled and a middle fraction taken at 167°C. (164-6°, 775.)

2.5.0 Syntheses of aliphatic cyclic phosphates.

2.5.1 2-Chloro-1,3,2-dioxaphospholane[55].

Redistilled phosphorus trichloride (22.0ml.,0.25 mole) was placed in a three necked flask, fitted with a stirrer and dropping funnel with calcium chloride guard tubes. Methylene chloride (50ml) was added, and ethylene glycol (139ml., 0.25mole) added dropwise from the dropping funnel. The mixture was stirred until evolution of hydrogen chloride ceased, and excess methylene chloride was removed on the rotary evaporator. The product was distilled under reduced pressure, and obtained as a clourless fuming liquid. B.pt. 45°C. at 15mm Hg. (28.2g., 89%) (56°, 25mm[55]).

Chlorine analysis for $C_2H_4ClO_2P$

Requires 28.06%

Found 28.3%

2.5.2 2-Methoxy-1,3,2-dioxaphospholane[55].

2-Chloro-1,3,2-dioxaphospholane (12.65g., 0.1mole) was dissolved in anhydrous ether (50ml.). Pyridine (11.8g., 0.15mole) was added and the mixture cooled in an ice salt bath to -5°C. Methanol (3.2g., 0.1mole) was added dropwise with stirring, after

the addition of methanol the reaction mixture was allowed to warm to room temperature. The pyridinium hydrochloride was filtered, and the residue distilled. B.pt. 54°C. at 25mm Hg. (54°,25mm) (10g.,81%). The distilled material contained traces of pyridinium hydrochloride , this was removed by pouring the product in to anhydrous benzene, followed by filtration. Distillation gave an analytically pure product.

Mass spectrum

P^+ m/e 122.

2.5.3 2-Isopropoxy-1,3,2-dioxaphospholane.

2.5.4 2-Phenoxy-1,3,2-dioxaphospholane.

2.5.5 2-t-Butoxy-1,3,2-dioxaphospholane.

2.5.3, 2.5.4, and 2.5.5 were prepared in a similar manner to 2.5.2 , using mole equivalents of alcohol (or phenol) and chlorophosphite. Table III shows yields and analytical data for these compounds.

Table III

Compound	B.pt. °C	Lit.[55]	n.m.r. ($CDCl_3$+TMS)	m/s
2.5.3.	65°/24mm	69°/25mm	τ 8.8, d, 6H. τ 5.8, s, 2H. τ 4.0, d, 2H. τ 4.0, m, 1H.	P^+
2.5.4.	72°/24mm	73°/25mm	τ 2.9, s, 5H. τ 5.9, s, 2H. τ 6.0, d, 2H.	P^+
2.5.5.	72°/15mm	84°/25mm	τ 6.0, s, 2H. τ 6.1, d, 2H. τ 2.3, s, 9H.	P^+

2.5.6 2-Chloro-2-oxo-1,3,2-dioxaphospholane [56].

2-Chloro-1,3,2-dioxaphospholane (25.3g ,0.2mole) was dissolved in anhydrous benzene (150ml.). Dry oxygen was passed through the stirred solution, and an exothermic reaction followed. The mixture refluxed but no attempt was made to moderate the reaction. The reaction mixture was allowed to cool to room temperature, and excess benzene evaporated. (Total reaction time = 5 hours). Distillation of the residue gave a liquid. B.pt. 79°/ 0.4mm Hg. (20g.,70%) (Lit. 79°, 0.4mm).

Chlorine analysis for $C_2H_4ClO_3P$

Requires	24.9%
Found	25.4%

I.R. data

2980cm^{-1}	CH stretch
1300cm^{-1}	P=O stretch
1020cm	O-P stretch

2.5.7 2-Methoxy-2-oxo-1,3,2-dioxaphospholane.

Method I [57]

2-Methoxy-1,3,2-dioxaphospholane (12.2g.,0.1mole) was dissolved in anhydrous methylene chloride (50ml.). The solution was cooled to -80°C by means of a cardice-acetone bath, and with the total exclusion of moisture, a solution of dinitrogen tetroxide (10%) was added dropwise with stirring, until the solution turned green.

Evaporation of the solution gave an oil B.pt. 98°C at 1mm Hg. (Lit. 89-92°, 0.6mm [57]) (5.8g., 42%). Colourless extremely hygroscopic oily liquid.

n.m.r. ($CDCl_3$ + TMS)

τ 6.2, d, J = 12Hz, 3H

τ 5.55, d, J = 11Hz, 4H

I.R.

1290cm^{-1} P=O stretch

1030cm^{-1} P-O-(alkyl) stretch

microanalysis for $C_3H_7O_4P$	C	H	P
Requires	26.08	5.07	22.46
Found	26.2	5.31	23.00

2.5.7 Method II

2-Chloro-2-oxo-1,3,2-dioxaphospholane (14.2g.,0.1mole) was dissolved in dry chloroform (50ml.). Anhydrous sodium carbonate (12g., 0.11mole) was added, and the mixture agitated at -10°C. Methanol (3.2g.,0.1mole) was added dropwise to the stirred solution. After 2.5 hr. the reaction mixture was filtered, and the filtrate evaporated in vacuo. Distillation gave a liquid B.pt. 98°C at 1mm Hg (12g., 86%). Analytical data identical to Method I.

2.5.8 2-Isopropoxy-2-oxo-1,3,2-dioxaphospholane.

2-Isopropoxy-1,3,2-dioxaphospholane was oxidized in a similar manner to 2.5.7, using dinitrogen tetroxide. B.pt.60°C. at 0.2mm. Hg (12g., 72%).

n.m.r. ($CDCl_3$ + TMS)

τ 8.6, d, 6H , J = 10Hz

τ 5.5, m, 5H

I.R.

1280cm^{-1} , 1030cm-1.

microanalysis for $C_5H_{11}O_4P$	C	H	P
Requires	36.14	6.62	18.67
Found	35.91	6.25	19.00

2.5.9 Bis-(2-oxo-1,3,2-dioxaphospholane)-2-oxide (58).

Phosphorus pentoxide (28g., 0.2mole) was weighed in to a three necked flask under dry nitrogen in a glove bag. Chloroform (200ml.) was added, and the mixture was refluxed under nitrogen. Ethylene oxide (17.6g., 0.4mole) was dissolved in anhydrous chloroform (50ml.) and added dropwise to the refluxing mixture. After the addition, most of the phosphorus pentoxide had dissolved, and the hot solution was rapidly filtered through a glass wool plug. The solution was reduced to half its volume by evaporation, and the resulting solution was cooled in an ice bath in the absence of air. Crystals were deposited and filtered under nitrogen, washed with anhydrous chloroform and dried. m.pt. 120°C. (18g., 39%)

n.m.r. ($DMSO_{d6}$ + TMS)

τ 5.76, d, J = 11Hz

I.R. (KBr disc)

1290cm^{-1} P=O stretch.

Microanalysis for $C_4H_8O_7P_2$	C	H	P
Required	20.86	3.48	26.9
Found	21.12	3.21	27.41

2.5.10 2- Phenoxy-2-oxo-1,3,2-dioxaphospholane[59].

Redistilled ethylene glycol (12.4g., 0.2mole) was dissolved in pyridine (15ml.) and added dropwise to phenyl phosphodichloridate[60] (41.2g., 0.2mole) in dry benzene (100ml.) at 20°C under nitrogen. The solution was heated to 40°C for 1 hr.,poured in to ether and filtered. Evaporation followed by distillation under reduced pressure gave a fraction B.pt. 153°/ 3mm Hg.

(Lit. 154°/ 3mm Hg.) m.pt. 30°C (19g., 47%)

n.m.r. ($CDCl_3$ + TMS)

τ 5.5, d, 2H , J = 6Hz

τ 5.8, s, 2H

τ 8.8, s, 5H

I.R.

1300cm^{-1}, 1029cm^{-1}, 1600cm^{-1} .

Mass spectrum

P^+ m/e 200.

2.5.11 2-t-Butoxy-2-oxo-1,3,2-dioxaphospholane.

Method I

2-t-Butoxy-1,3,2-dioxaphospholane (1.64g., 0.01mole) was dissolved in dry benzene (30ml.). Yellow mercuric oxide (6g.) was

added and the suspension stirred at room temperature for three days. The solution was filtered and the residue concentrated in vacuo, yielding an oily liquid.

n.m.r. ($CDCl_3$ + TMS)

τ 8.5, s, 9H

τ 5.5, m, 4H

I.R.

1290cm^{-1} , 1030cm^{-1} .

Phosphorus analysis for $C_6H_{13}O_4P$

	P
Requires	17.22
Found	16.81

2.5.12 2-Hydroxy-2-oxo-1,3,2-dioxaphospholane.

Method I

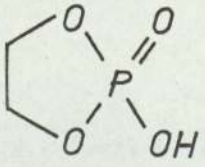
Bis-(2-oxo-1,3,2-dioxaphospholane)-2-oxide (2.3g., 0.01mole) was dissolved in warm anhydrous tetrahydrofuran (50ml.) in a three necked flask, under dry nitrogen. A solution of water in tetrahydrofuran (1.8g./ 100ml.) (10ml.) was added to the solution, with stirring over a period of 2hr. Excess solvent was evaporated yielding a crystalline substance m.pt. 125°C. (2g., 80%).

n.m.r. ($DMSO_{d6}$ + TMS)

τ 5.7, d, J = 11Hz, 4H

τ -1.9, s, 1H

supporting



I.R. (KBr disc)

2700cm^{-1} , br, OH stretch

1300cm^{-1} , P=O stretch

Mass spectrum

P^+ m/e 124 , 94 , 80.

Microanalysis for $C_2H_4O_4P$	P	H	C
Requires	25.00	4.03	19.35
Found	24.29	4.0	19.20

2.5.12 Method II

2-Chloro-2-oxo-1,3,2-dioxaphospholane (1.42g., 0.01mole) was dissolved in benzene (20ml.). A solution of water in tetrahydrofuran was added slowly with vigorous stirring (0.9g. / 50ml.) (10ml.). The solution was allowed to stand for 2hr. during which time the solution deposited crystals. The crystals were filtered under nitrogen, washed with tetrahydrofuran and dried under vacuum. m.pt. 120-30°C. Analytical data identical to Method I.

2.5.12 Method III

2-t-Butoxy-2-oxo-1,3,2-dioxaphospholane (1.8g., 0.01mole) was heated to 100°C. under vacuum, isobutene was evolved leaving a white crystalline mass. m.pt. 125°C (T.H.F.).

Analytical data identical to 2.5.12 Method I.

2.5.13 2-Oxo-2-phenoxy-4,5-dimethyl-1,3,2-dioxaphospholane.

Butane-2,3-diol (9.0g., 0.1mole) was dissolved in pyridine

(16g.,0.21mole) and added dropwise to a stirred solution of phenyl phosphodichloridate (21.1g., 0.1mole) in benzene (100ml.), over a period of ½hr. The solution was heated to 50°C. for 2hr., poured in to ether and filtered. Excess ether was removed in vacuo, and the residue distilled B.pt. 160°C at 0.3mm Hg. m.pt. 65°C. (Lit. 66°C.) (14g., 62%).

n.m.r. ($CDCl_3$ + TMS)

τ 2.65, s, 5H

τ 5.5, m, 2H

τ 8.6, m, 6H

I.R.

1600cm^{-1} C=C (arom.) , 1400cm^{-1} Me def. (d)

1290cm^{-1} P=O stretch , 1220, P-Ø stretch

Mass spectrum

P^+ m/e 228.

2.5.14 2-Oxo-2-phenoxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane.

Phenylphosphodichloridate (21.1g., 0.1mole) was dissolved in benzene (100ml.). A solution of anhydrous pinacol (11.8g., 0.1mole) in pyridine (16g.,0.202mole) was added dropwise to the stirred dichloridate at room temperature. The reaction mixture was maintained at 50°C. for 15 hr. with stirring until the reaction was complete (T.L.C.) .The product was poured in to dry ether, filtered and the residue evaporated, yielding a solid. m.pt.106°C. (Et_2O) (Lit.107°) (21g., 82%).

n.m.r. ($CDCl_3$ + TMS)

τ 8.5, s, 12H

τ 2.9, s, 5H

I.R.

P=O 1290cm^{-1}

P−Oϕ 1220cm^{-1}

C=C 1600cm^{-1}

$C(CH_3)_2$ sym. doublet 1400cm^{-1}

CH arom. 3010cm^{-1}

Mass spectrum

P^+ m/e 256 , 241.

2.5.15 4-Methyl-2-oxo-2-phenoxy-1,3,2-dioxaphospholane.

4-Methyl-2-oxo-2-phenoxy-1,3,2-dioxaphospholane was prepared in an analogous manner to 2.5.10 (132-5°, 0.1) Lit. B.pt. 134°, 0.1.mm

n.m.r. ($CDCl_3$ + TMS)

τ 8.7, t, 3H τ 6.0, m, 3H

τ 3.0, s, 5H

I.R.

1290cm^{-1} P=O , 2980cm^{-1} CH , 1225cm^{-1} P−Oϕ stretch.

Mass spectrum

P^+ m/e 214.

2.5.16 2-t-Butoxy-2-oxo-4-methyl-1,3,2-dioxaphospholane.

2-t-Butoxy-2-oxo-4-methyl-1,3,2-dioxaphospholane was prepared

in an analogous manner to 2.5.11, from 2-t-Butoxy-4-methyl-1,3,2-dioxaphospholane[55] B.pt. 77°C. / 25mm Hg., by dinitrogen tetroxide oxidation at -80°C.

n.m.r. ($CDCl_3$ + TMS)

τ 8.5, s, 9H τ 8.55, m, 3H

τ 5.5, m, 3H

I.R.

1400cm^{-1} Me def. (two bands), 1298cm^{-1} P=O

Microanalysis for $C_7H_{15}O_4P$	P
Requires	15.97%
Found	15.58%

2.5.17 2-t-Butoxy-2-oxo-4,5-dimethyl-1,3,2-dioxaphospholane.

2-t-Butoxy-4,5-dimethyl-1,3,2-dioxaphospholane (prepared in a similar manner to 2.5.5) (19.2g., 0.1mole) was dissolved in anhydrous chloroform (100ml.), and cooled to -80 C. by means of an acetone / cardice bath, in the absence of moisture. Dinitrogen tetroxide solution (10% in $CHCl_3$) was added dropwise to the phosphite with stirring, until a green colour developed. Excess solvent was removed in vacuo, and the product dried under high vacuum. (18g., 86%).

n.m.r.

τ 8.5, m, 15H

τ 5.3, m, 2H

I.R.

$1045cm^{-1}$	P—OC stretch	$1400cm^{-1}$	Me def.
$2980cm^{-1}$	CH stretch	$1300cm^{-1}$	P=O

Microanalysis for $C_8H_{17}O_4P$	P
Requires	14.90%
Found	14.61%

2.5.18 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane[60].

Anhydrous pinacol (59g., 0.5mole) was dissolved in anhydrous ether (300ml) containing pyridine (82g., 1.03mole) in a dry three necked flask, fitted with a stirrer, nitrogen inlet, and dropping funnel. The solution was cooled to -10°C. by means of an ice salt bath. Phosphorus trichloride was added dropwise to the stirred solution over a period of 2hr. The reaction mixture was refluxed for 1hr., cooled and filtered. The filtrate (a yellow fuming oil) was distilled under reduced pressure B.pt.46°/ 2mm Hg. (Lit. 53°/ 3mm[60]) (32g., 35%).

2.5.19 t-Butoxy-2-oxo-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane.

t-Butoxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane[60] (2.2g., 0.01mole) was dissolved in anhydrous chloroform (25ml.). Dinitrogen tetroxide in chloroform was added to the phosphite solution at -80°C. with stirring, until a green colour developed. Evaporation of the solvent gave colourless crystals m.pt. 60°C. Vacuum sublimation of the product at 0.1mm gave a white solid

m.pt. 72°C. (Lit.[60] 71°C.) (2g., 90%).

n.m.r.

τ 8.6, s, 9H

τ 8.5,s, 12H

I.R.

1028cm^{-1} , 1290cm^{-1}

Microanalysis for $C_{10}H_{21}O_4P$	P
Requires	13.35%
Found	13.16%

2.5.20 2,2,2- Trimethoxy-4,5-dimethyl-1,3,2-dioxaphosphol- Δ^4-ene.

Trimethyl phosphite (124g., 1mole.) was dissolved in dry benzene (100ml.). Redistilled diacetyl (86g., 1mole) in dry benzene (30ml.) was added dropwise with stirring. The yellow colour of the diacetyl disappeared, and excess benzene was removed in vacuo. The product was distilled in vacuo B.pt. 60°/1mm Lit.45°/05mm[61a])

n.m.r. ($CDCl_3$ + TMS)

τ 8.2, s, 6H

τ 4.4, d, 9H, J = 14Hz.

2.5.21 2,2,2 -Trimethoxy-4,5-diphenyl-1,3,2-dioxaphosphol- Δ^4-ene.

Trimethyl phosphite (124g., 1mole) was dissolved in dry benzene, and heated to 40 C. under nitrogen. Benzil (210g., 1mole) was added and the mixture stirred for 4 hr. Excess benzene was removed in vacuo, and the product recrystallized from ether m.pt. 84°C.

(Lit. 72°).

n.m.r. ($CDCl_3$ + TMS)

τ 6.5, d, 9H, J = 15Hz

τ 2.8, m, 10H

2.5.22 2-Methoxy-2-oxo-4,5-dimethyl-1,3,2-dioxaphospholene.[117]

2.5.20 (21.0g., 0.1mole) was dissolved in anhydrous chloroform, and cooled to -10°C. by means of an ice-salt bath. Water (1.8g., 0.1mole) was added dropwise to the stirred solution. The chloroform was removed in vacuo and the residue distilled, yielding a viscous gum which solidified on cooling (4g., 24%) m.pt. 42°C. (Lit. 43°C.).

2.6.0 Synthesis of aromatic cyclic phosphate esters.

2.6.1 2-Chloro-4,5-benzo-1,3,2-dioxaphospholane[61].

Phosphorus trichloride (150g., 1.09mole) was added to moist* catechol (80g., 0.72mole) contained in a 500ml.flask fitted with a reflux condensor. After a vigorous evolution of hydrogen chloride (ca 1½ hr.),phosphorus trichloride (60g., 0.4mole) was added, and the mixture was refluxed for 3 hr. The product was distilled under reduced pressure 86°/ 15mm Hg. (Lit. 91°/ 18mm), and solidified on cooling. (82g., 65%).

* Addition of water (ca. 1g.) is required; if this is omitted the course of the reaction is altered.

2.6.2 2,2,2-Trichloro-4,5-benzo-1,3,2-dioxaphospholane[62].

Phosphorus pentachloride (208.5g., 1mole) was dissolved in dry benzene (500ml.), contained in a 1 litre flask. Catechol (100g., 0.9mole) was added little by little to the stirred solution over a period of 1 hr. The resulting solution was refluxed for 12 hr. Excess benzene was removed by evaporation in vacuo and the product distilled. B.pt. 132°C./ 15mm Hg. (168g., 76%). The product was isolated, pale green crystals fuming in moist air. m.pt. 62°C. (Lit. 61°C.[62]).

2.6.3 2-Chloro-2-oxo-4,5-benzo-1,3,2-dioxaphospholane[63].

2,2,2-Trichloro-4,5-benzo-1,3,2-dioxaphospholane (24.5g., 0.1mole) was placed in a 250ml. round flask, fitted for distillation. Acetic anhydride (10.2g., 0.1mole) was added dropwise in to the

flask, heated to 60°C. by means of a water bath. Acetyl chloride distilled over, and the theoretical amount was collected in the receiver. The residue in the distillation flask was distilled under reduced pressure in a Claisen Vigreux flask fitted with an air condensor. The distillation was difficult, as the product readily solidified in the condenser, and thus a hair dryer was used to heat the condenser. B.pt 84°C./ 0.1mm Hg. (Lit. 83-7°/ 0.1mm [63]) (14g., 73%).

Chlorine analysis for $C_6H_4O_3PCl$ Cl

Requires	18.63
Found	19.01

2.6.4. 2-Methoxy-2-oxo-4,5-benzo-1,3,2-dioxaphospholane.

Methanol (4g., 0.125mole) was dissolved in dry ether (25ml.), and added dropwise to a stirred solution of 2-chloro-2-oxo-4,5-benzo-1,3,2-dioxaphospholane (19g., 0.1mole) in ether (50ml.) under nitrogen. The solution was immediately evaporated and the residue distilled B.pt. 101°C./ 1mm Hg. (14.6g., 78.5%). The distillate solidified, on cooling, to white crystals m.pt. 60°C. (Lit. [62] 58°C.) ; the compound was found to be extremely hygroscopic.

n.m.r. ($CDCl_3$ + TMS)

τ 6.2, d, J = 12Hz

τ 3.0, s

I.R.

$1030cm^{-1}$ POC stretch, $1300cm^{-1}$ P=O stretch

$1600cm^{-1}$ C=C

Mass spectrum

P^+ m/e 186.

Microanalysis for $C_7H_7O_4P$	C	H	P
Requires	45.16	3.76	16.66
Found	44.82	3.98	18.42

2.6.5 2-Isopropoxy-2-oxo-4,5-benzo-1,3,2-dioxaphospholane.

2-Chloro-2-oxo-4,5-benzo-1,3,2-dioxaphospholane (19g., 0.1mole) was dissolved in anhydrous ether (150ml.). Triethylamine (12g., 0.12mole) was added, and the mixture cooled to 5°C. Isopropanol (6.5g., 0.11mole) was added dropwise to the stirred reaction mixture, and the precipitated triethylamine was filtered. Excess ether was removed by distillation, and the product distilled under reduced pressure B.pt. 92°/ 0.4mm Hg.. The distillate solidified at room temperature, but was extremely hygroscopic, converting to a liquid which did not solidify. The solid was therefore stored in ampoules under nitrogen, and handled in a glove bag. (15g., 70%)

n.m.r. ($CDCl_3$ + TMS)

τ 8.5, d, 6H, J = 10Hz

τ 4.9, m, 1H 2.75, s, 4H

I.R.

sym. doublet 1380cm^{-1}

1600cm^{-1} C=C aromatic

1300cm^{-1} P=O , 1050cm^{-1} P-O alkyl.

Mass spectrum

P^+ m/e 214.

Microanalysis for $C_9H_{11}O_4P$ P

Requires 14.48

Found 14.16

2.6.6 2-Phenoxy-2-oxo-4,5-benzo-1,3,2-dioxaphospholane (64).

2-Chloro-2-oxo-4,5-benzo-1,3,2-dioxaphospholane (19g., 0.1mole) was dissolved in anhydrous ether (100ml.)containing triethylamine (12g., 0.12mole). A solution of redistilled phenol in ether (9.4g., 0.1mole in 10ml.) was added dropwise to the stirred reaction mixture. The suspension was stirred for 1 hr. and filtered. The filtrate was concentrated in vacuo, and the residue distilled. B.pt. 170° at 0.1mm.. Redistillation gave a fraction B.pt. 160° at 0.06mm as an oily liquid.

(Lit. 161 / 0.07mm) (15g., 60%).

n.m.r. ($CDCl_3$ + TMS)

τ 2.9, s, 5H

τ 7.1, s, 4H

I.R.

$1600cm^{-1}$	C=C aromatic	$1210cm^{-1}$	P—Ø stretch
$1029cm^{-1}$	POC	$1300cm^{-1}$	P=O stretch

Mass spectrum

P^+ m/e 248.

Microanalysis for $C_{12}H_9O_4P$

	P
Requires	12.50
Found	12.12

2.6.7 2-Hydroxy-2-oxo-4,5-benzo-1,3,2-dioxaphospholane[65].

Phosphorus pentoxide (71g., 0.5mole) was fused with catechol (110g.,1mole) at 120°C. for 1 hr. Distillation under reduced pressure, using an air condensor, gave a viscous liquid B.pt. 238 / 1mm Hg. Redistillation gave a viscous oil B.pt. 230°/ 3mm Hg. (Lit[165] 225° / 3mm) (56g., 33%). Crystals at room temperature.

n.m.r. ($DMSO_{d6}$ + TMS)

τ	7.2, m, 4H	-1.0, s, 1H	

Mass spectrum

P^+ m/e 172.

2.6.8 O-Hydroxyphenylphosphate[65].

2-Hydroxy-2-oxo-1,3,2-dioxaphospholane was dissolved in the minimum of water. Extraction with boiling ethyl acetate, followed by addition of benzene gave a crystalline deposit m.pt. 139-41°C.

(Lit.[65] 139°C.)

n.m.r. ($DMSO_{d6}$ + TMS)

τ 7.1, s, 4H τ 0.0, m, 3H

2.6.9 2-t-Butoxy-2-oxo-4,5-benzo-1,3,2-dioxaphospholane.

2-t-Butoxy-2-oxo-4,5-benzo-1,3,2-dioxaphospholane was prepared in an analogous way to 2.6.5 using redistilled t-Butanol. The product was a solid which readily gave off isobutene gas, to leave 2.6.7. The product was too unstable for micro-analysis, but n.m.r. was obtained.

n.m.r. ($DMSO_{d6}$ + TMS)

τ 7.0, s, 4H

τ 2.5, s, 9H

2.6.10 2-Cumyloxy-2-oxo-4,5-benzo-1,3,2-dioxaphospholane.

2-Cumyloxy-2-oxo-4,5-benzo-1,3,2-dioxaphospholane was prepared in an analogous way to 2.6.5 using redistilled cumyl alcohol. The product was extremely unstable, giving α-methyl styrene and 2.6.7 very rapidly at room temperature.

2.6.11 2-Phenoxy-2-oxo-4,5-benzo-1,3,2-dioxaphosphorinone[66].

Saligenin (12.4g., 0.1mole) was dissolved in anhydrous chloroform (150ml.) contained in a 500ml. three necked flask, fitted with a reflux condensor, dropping funnel, and nitrogen inlet. Anhydrous sodium carbonate was added (12g.,0.11mole) and copper powder (0.1g.). Phenylphosphdichloridate (21.1g.,

0.1mole) was added to the stirred reaction mixture. An exothermic reaction followed, and after 2 hr., the reaction mixture was refluxed for a further 2 hr. The reaction mixture was filtered, and the filtrate concentrated in vacuo. The product was recrystallized from diethyl ether (11g., 42%) m.pt. 78°C. (Lit.[66] 77-9°).

n.m.r. ($CDCl_3$ + TMS)

τ 4.4, s, 1H

τ 4.9, d, 1H , J =3Hz 2.9, m, 9H

I.R. (KBr)

1225cm^{-1} P−Oϕ stretch 1600cm^{-1} C=C

2.6.12 2-(3-Hydroxy-2-naphthyloxy)-4,5-naphtho-1,3,2-dioxaphospholane.

Naphthalene-2,3-diol (16g., 0.1mole) was refluxed with phosphorus trichloride (6.8g., 0.05mole) in the absence of moisture. After 1 hr. phosphorus trichloride (6.8g., 0.05mole) was added, and the mixture allowed to stand at room temperature for ½ hr. The reaction mixture was poured in to methanolic ether (3.2g. / 100ml.), and stirred for a further ½ hr., during which time a precipitate formed. The crystalline precipitate was washed with anhydrous ether, and dried in vacuo m.pt. 220°C.

n.m.r. ($DMSO_{d6}$ + TMS)

τ 3.8, m, 12H τ 7.4, s, 1H

Mass spectrum

P^+ m/e 348.

I.R.

1600cm^{-1} C=C aromatic 1020cm^{-1} P−O stretch

Microanalysis for $C_{20}H_{13}O_4P$	C	H	P
Requires	68.96	3.73	8.91
Found	68.69	3.42	9.21

2.7.0 Synthesis of metal chelates derived from aromatic cyclic phosphates.

2.7.1 Tris-(catechol phosphate) iron III.

Method I

2-Methoxy-2-oxo-4,5-benzo-1,3,2-dioxaphospholane (10g., 0.054mole) was heated to 120°C. in a round flask (50ml.) in an oil bath with vigorous stirring and total exclusion of moisture. Ferric chloride (anhydrous) (1.62g., 0.01mole) was added, and the mixture was stirred for 2 hr. Methyl chloride was evolved, leaving a yellow paste. The product was shaken with diethyl ether and filtered. The powdery crystalline product was washed with five aliquots of anhydrous ether, (5 x 20ml.) under dry nitrogen. The product was dried in vacuo (4.2g., 73%).

I.R.

1210cm^{-1} P=O → Fe 1600cm^{-1} C=C stretch.

Microanalysis for $C_{18}H_{12}FeO_{12}P_3$	P%
Requires	16.34
Found	16.34

2.7.1 Method II

2-Isopropyl-2-oxo-4,5-benzo-1,3,2-dioxaphospholane was used for the preparation of 2.7.1 instead of 2-methyl-2-oxo-4,5-benzo-1,3,2-dioxaphospholane, to give a higher yield of 2.7.1 (84%) and a faster reaction time (15 min.).

2.7.2 Tris-(catechophosphate)-Vanadium III.

2-Isopropyl-2-oxo-4,5-benzo-1,3,2-dioxaphospholane (7g., 0.032mole) was heated with anhydrous vanadium trichloride (1.5g., 0.01mole) to yield a bluish-grey paste. Extraction with ether followed by filtration gave the required product which was handled under nitrogen and stored in sealed tubes (2.6g., 46%).

I.R.

1200cm^{-1} P=O stretch 1600cm^{-1} C=C stretch.

Microanalysis for $C_{18}H_{12}O_{12}P_3V$	P
Requires	16.48
Found	16.20

2.7.3 Attempted preparation of a molybdenum-catechol cyclic phosphate complex.

2-Methoxy-2-oxo-4,5-benzo-1,3,2-dioxaphospholane (10g., 0.53mole) was heated with molybdenum pentachloride (2g., 0.007mole) to 120 C for 2 hr. Extraction with ether gave a brown solid, which proved to be extremely hygroscopic. Microanalysis showed the presence of two phosphate groups and the formula $MoO_2(C.C.P.)_2^*$ was tentatively assigned.

*C.C.P. = Catechol cyclic phosphate

2.8 Miscellaneous Preparations.

2.8.1 Ethylbenzene Hydroperoxide.

Ethylbenzene Hydroperoxide (EBHP) was prepared by a modified method of that used by Kharasch[50]. Hydrogen Peroxide (HTP) (250ml., 85%), was placed in a 1 litre three necked flask, fitted with a mechanical stirrer, dropping funnel, thermometer, and ice bath. The flask was cooled to -10°C. by means of an ice-salt mixture, and sulphuric acid (1 drop) was added. Phenyl ethanol (122g., 1mole) was added dropwise to the stirred acidified HTP, and the reaction mixture was allowed to stir over night. The product was poured in to water, and extracted with ether. The ether extract was washed and dried over anhydrous sodium carbonate. The solution was filtered, and excess ether was removed by vacuum distillation at room temperature. The product was dissolved in petroleum ether (200ml.) and added to a cold solution of sodium hydroxide (40g., 1mole) in water (100ml.). The solution was vigorously stirred, and the precipitate of the sodium ethylbenzene hydroperoxide filtered and washed with 2% sodium hydroxide solution. The precipitate was added to water (500ml.) and cardice chips were added. The free hydroperoxide was extracted with ether, washed with sodium bicarbonate solution, and dried. Excess ether was removed in vacuo, and the remaining hydroperoxide distilled in vacuo.

B.pt. 49° C. at 0.2mm Hg. (Lit. 47.2°[50] at 0.2mm).

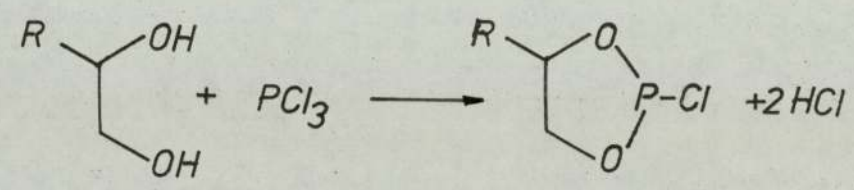
2.8.2 Phenylphosphodichloridate.

Phenol (94g., 1mole) was dissolved in phosphoryl chloride (600ml.). The solution was refluxed for 10 hr., with potassium chloride (1g.). Excess phosphoryl chloride was removed in vacuo, and the residue distilled. B.pt. 115°/ 10mm Hg. (Lit.[102] 106-7°, 7).

3.0 SYNTHETIC METHODS -

Results and discussion.

3.1. The interaction of aliphatic and aromatic diols with phosphorus halides is a very interesting topic and deserves some discussion here. Lucas et al.[51] prepared 2-chloro-1,3,2-dioxaphospholane in yields varying from 10 - 80%, and it was found that pure solvent gave higher yields of product. In our hands, the key to success proved to be high dilution; ethylene glycol was added slowly to phosphorus trichloride in chloroform, resulting in 90% yields of ethylene chlorophosphite. (16).

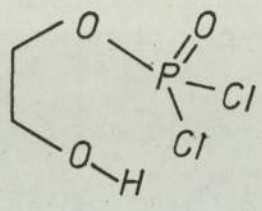


(16)

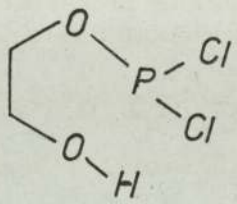
If the above precautions are not taken, high boiling polymeric material is usually formed.

Although workers claim to have prepared 2-chloro-2-oxo-1,3,2-dioxaphospholane by the reaction of phosphorus oxychloride with ethylene glycol[52], Edmundson has shown the reaction is not successful[53]. However in general, aliphatic and alicyclic diols react with PCl_3, $POCl_3$ and $PSCl_3$ to produce cyclic phosphorus esters[53], but the reaction is more difficult passing through the series. This agrees with the present study

and may be due to the intermediate dichlorohydroxyphosphorus ester. One hydroxyl group in ethanediol is almost always completely attacked before the other reacts, thus at first ethanediol acts as a monohydric alcohol,(53) and for the reactions described two intermediates may be obtained, a and b.

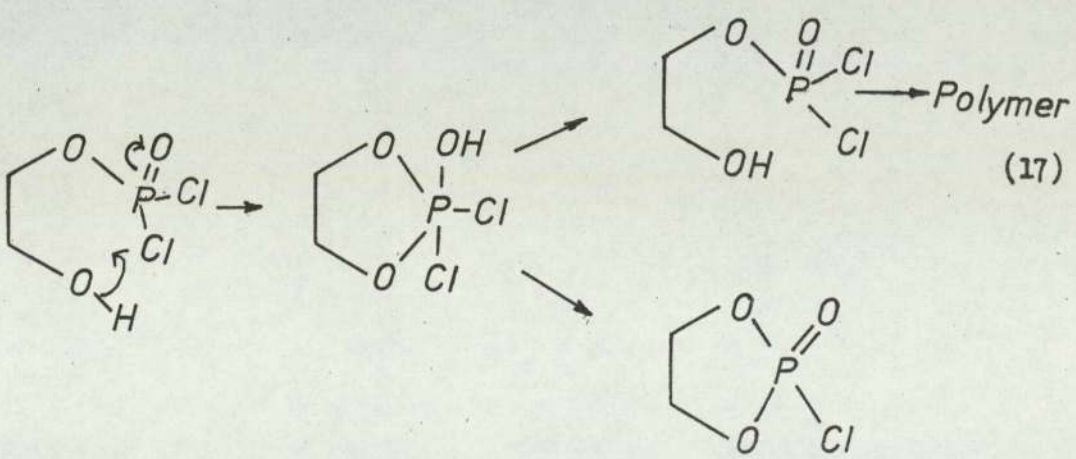


(a)



(b)

In case (a) the steric rquirements for reaction are more severe than in (b), thus it is more probable for (b) to form a cyclic phosphite than for (a) to form a cyclic phosphate. Another argument is that in case (a) if a five coordinate phosphorus species were formed (17) this should lack ring strain(37) however loss of chlorine would introduce ring strain, thus ring closure is not favoured and polymerisation results.

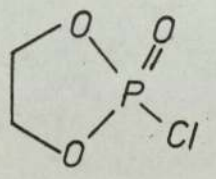


(17)

In case (b) loss of chlorine leads to ring formation without the possibility of a ring opened product.

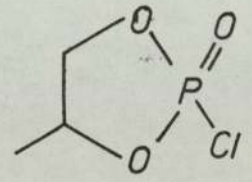
The oxidation of 2-chloro-1,3,2-dioxaphospholane with molecular oxygen [54] gave high yields 2-oxo-2-chloro-1,3,2-dioxaphospholane. The reaction was extended to other chlorophosphites, and it was found that in benzene solution the following chlorophosphates could be obtained. (18).

$$R-P-Cl \xrightarrow[O_2]{\text{ØH}} R-P(=O)-Cl \qquad (18)$$



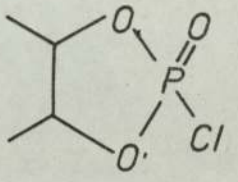
85% Yield

2-chloro-2-oxo-1,3,2-dioxaphospholane
(ethylene chlorophosphate)



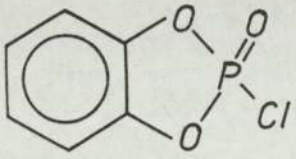
80% Yield

2-chloro-4-methyl-2-oxo-1,3,2-dioxaphospholane



50% Yield

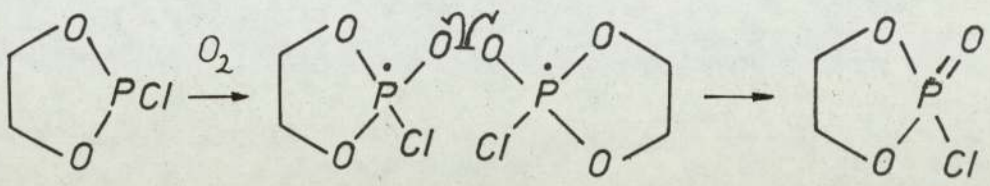
2-chloro-4,5-dimethyl-2-oxo-1,3,2-dioxaphospholane



30% Yield

2-chloro-2-oxo-4,5-benzo-1,3,2-dioxaphospholane (catechol chlorophosphate)

The low yield of catechol chlorophosphate compared with ethylene chlorophosphate may be due to the relative ease of formation of an intermediate phosphoranyl radical as follows, (19),

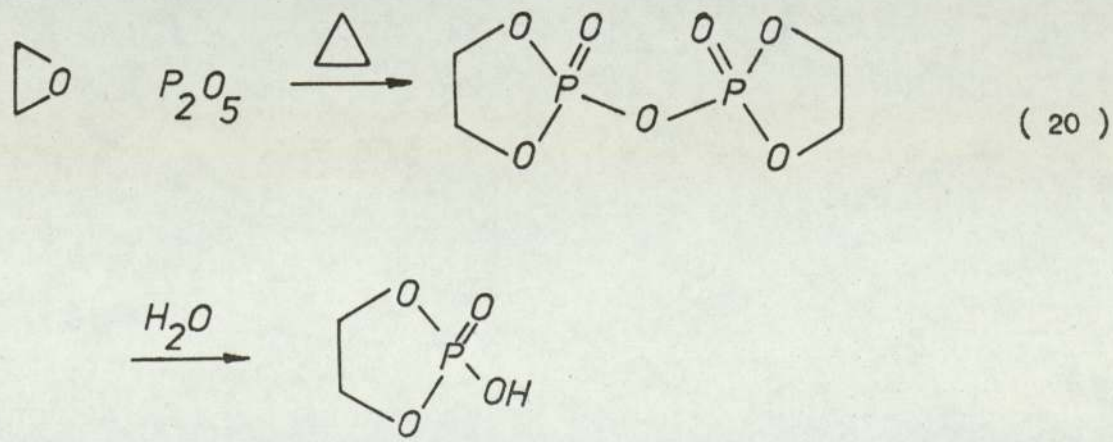


(19)

and for catechol chlorophosphate this may be more difficult, and explain the lower yields observed.

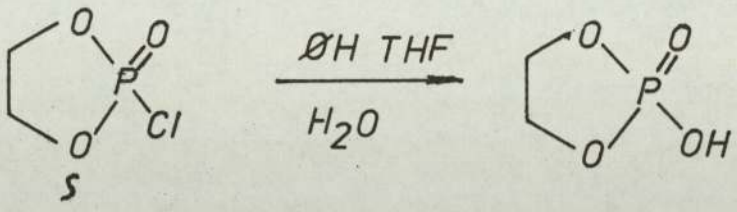
3.2 Acid cyclic phosphates.

The preparation of the simplest cyclic phosphate of the aliphatic series (2-hydroxy-2-oxo-1,3,2-dioxaphospholane), presented the greatest difficulty; two methods of preparation were developed, and a third literature method proved successful (58). The reaction of ethylene oxide with phosphorus pentoxide in chloroform gave ethylene pyrophosphate; hydrolysis of the pyrophosphate gave ethylene cyclic phosphate (20).



(20)

The hydrolysis had to be carefully controlled, because ring opened products and polymers can be formed. It was found that contrary to the literature[67] 2-hydroxy-2-oxo-1,3,2-dioxaphospholane (ethylene cyclic phosphate) could be prepared by hydrolysis of 2-chloro-2-oxo-1,3,2-dioxaphospholane (*S*) in THF / benzene; no other solvent (21)

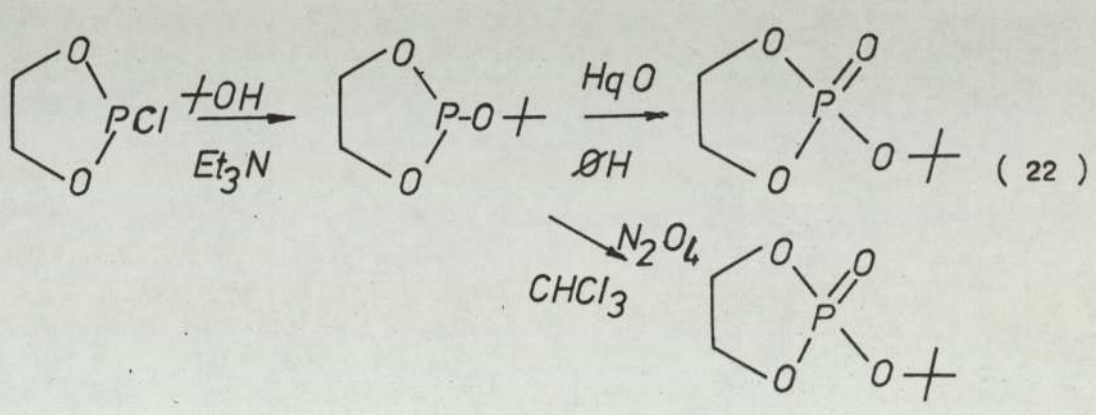


(21)

combination appeared to work.

The preparation of 2-t-butyl-2-oxo-1,3,2-dioxaphospholane was attempted in order to study the effect of a bulky group on the rate of reaction with hydroperoxide.

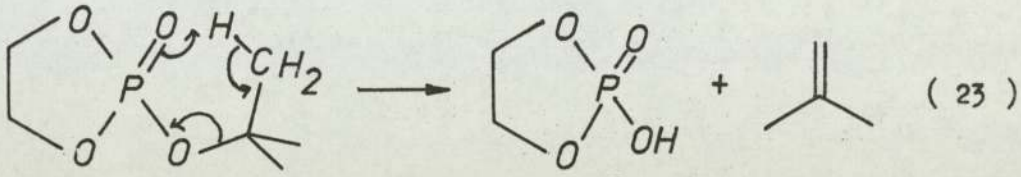
The t-butyl ester was prepared in two ways. (22).



(22)

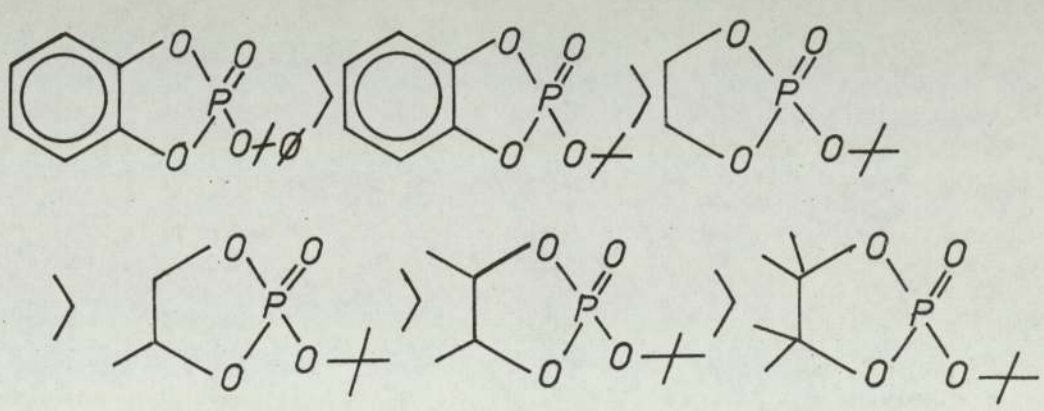
The product was an oily liquid, and the structure was confirmed by I.R., n.m.r., m/s and microanalysis for phosphorus. The compound decomposed slowly at room temperature, and the n.m.r. spectrum

gave a doublet at τ 8.7 indicating the presence of isobutene (Fig. V). Heating the phosphate under slight vacuum gave quantitative yields of isobutene and ethylene cyclic phosphate (23).



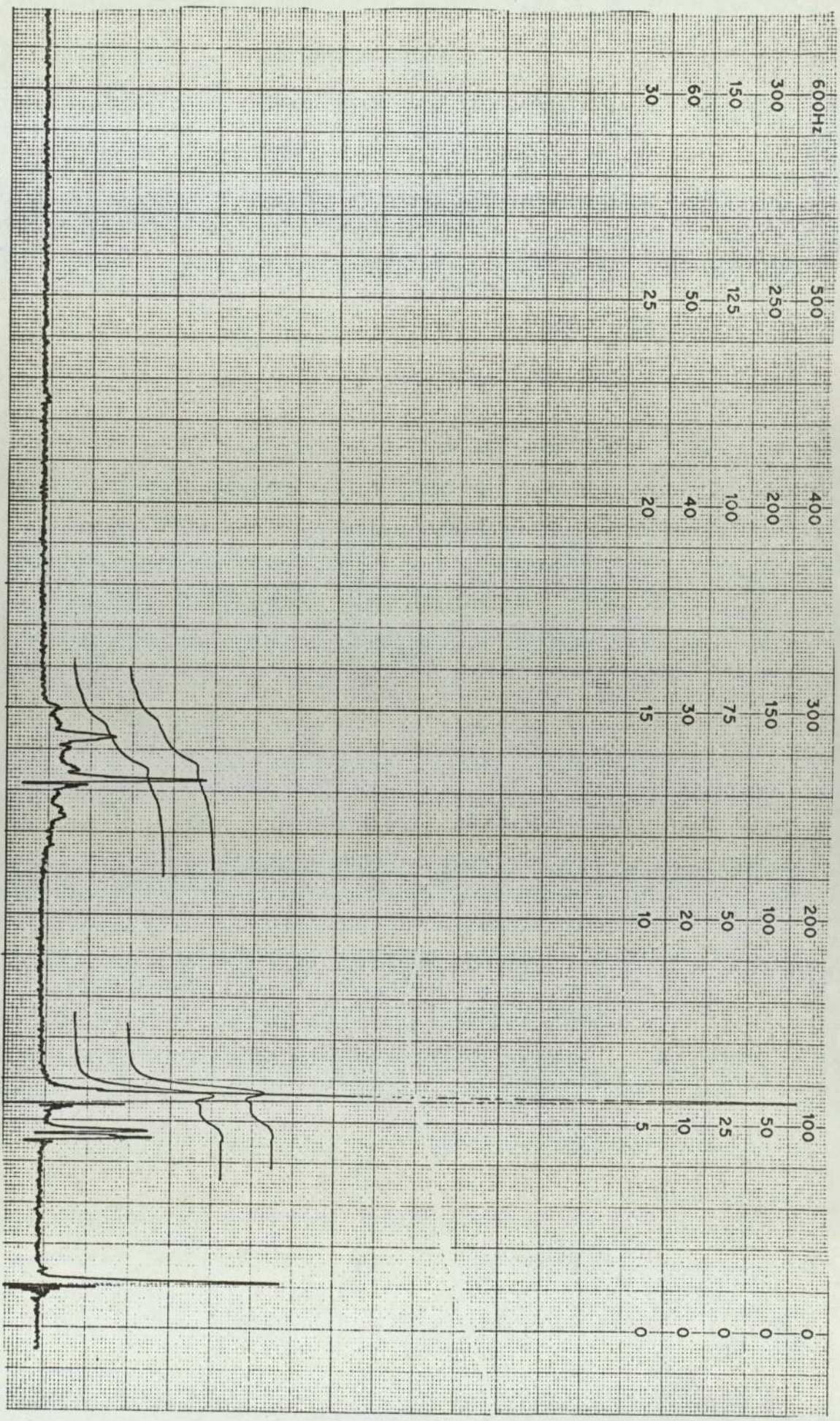
(23)

Stepwise addition of methyl groups in the dioxaphospholane ring retarded the decomposition rate; t-butyl pinacol cyclic phosphate was obtained as a crystalline solid (60) stable to sublimation under vacuum. All the decomposition reactions showed first order kinetics, the reaction probably proceeds by a unimolecular mechanism (23). A pattern emerged and the reaction rates appeared to be in the following order.



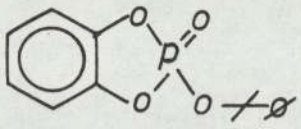
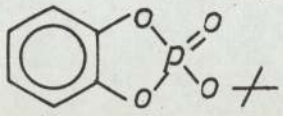
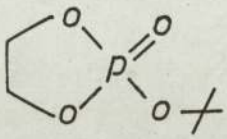
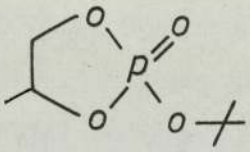
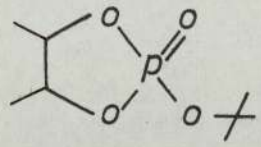
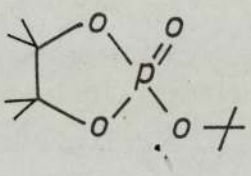
The rate of decomposition of 2-t-butoxy-2-oxo-1,3,2-dioxaphospholane at 53°C. approached that of t-butyl pinacol cyclic phosphate at 107°C. (Table IV).

Fig. V



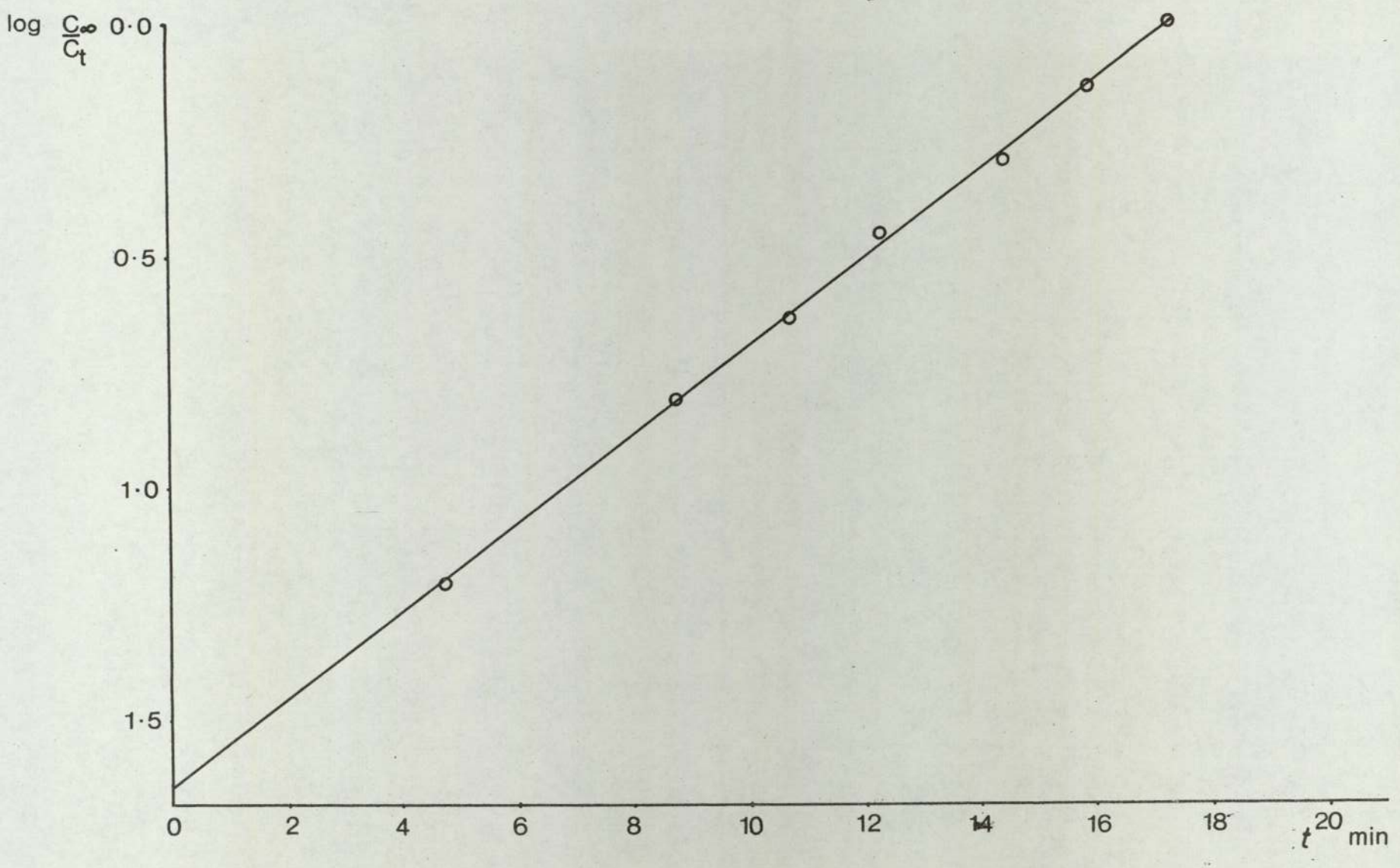
The H^1 n.m.r. spectrum of 2-t-butoxy-2-oxo-1,3,2-dioxaphospholane in $CDCl_3$

Table IV

Structure	K_1 sec.$^{-1}$	Temperature °C.
	-	-
	-	-
	3.56×10^{-3}	53
	4.14×10^{-3}	63
	3.68×10^{-3}	82
	2.76×10^{-3}	107

The reactions present a convenient route for the synthesis of cyclic acid phosphates which are difficult to prepare by standard methods. The +I effect of the methyl groups in the dioxaphospholane ring may account for the greater stability of t-butyl pinacol cyclic phosphate compared with t-butyl ethylene cyclic phosphate, because the transition state may be less ionic in nature than for the catechol derivatives. This supports the evidence for an ionic mechanism for the decomposition of hydroperoxide using catechol phosphates (14)(15)(16), whereas with 4,5-dimethyl-2-oxo-2-

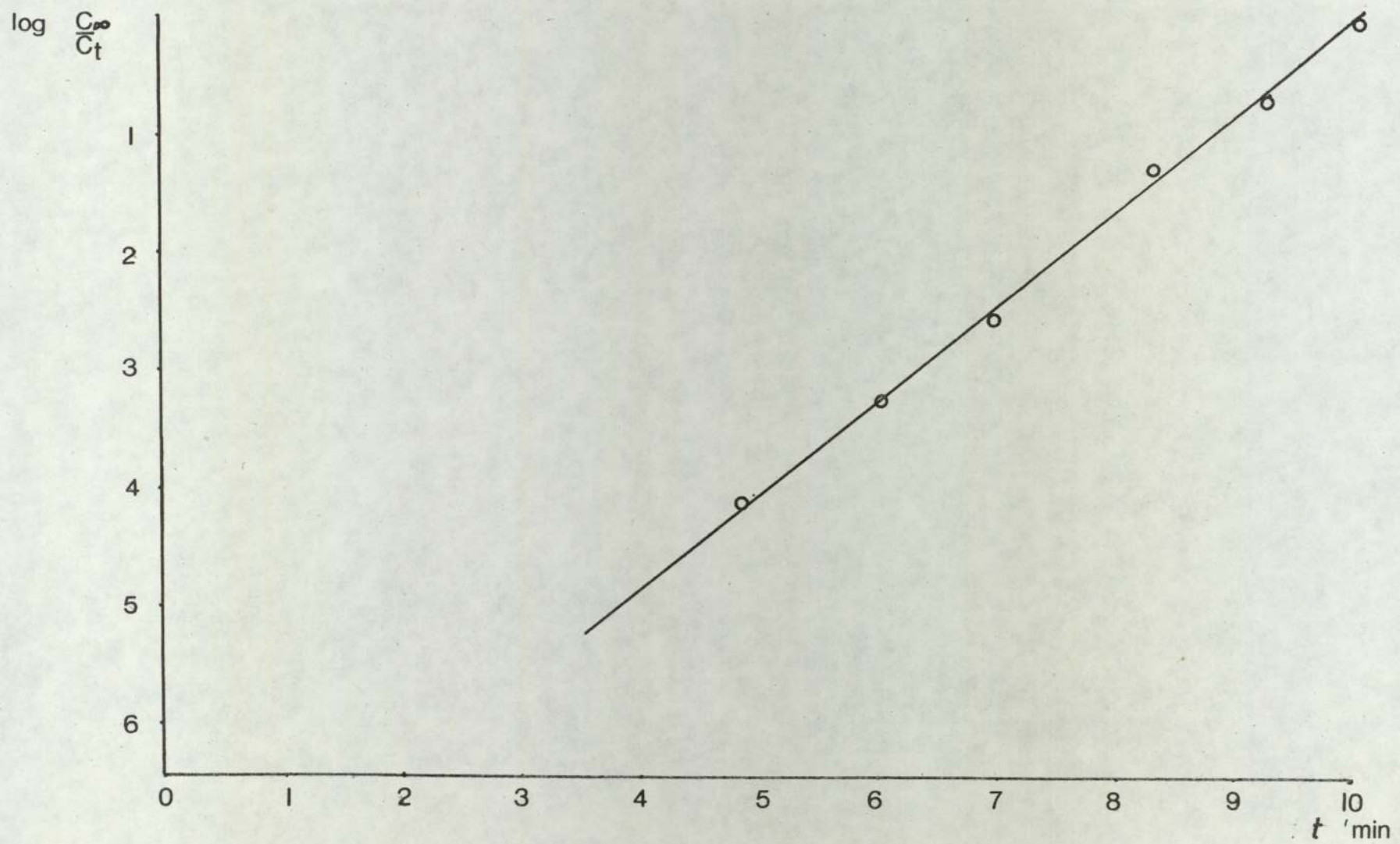
Fig VI



The decomposition of 2-t-butoxy-2-oxo-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane

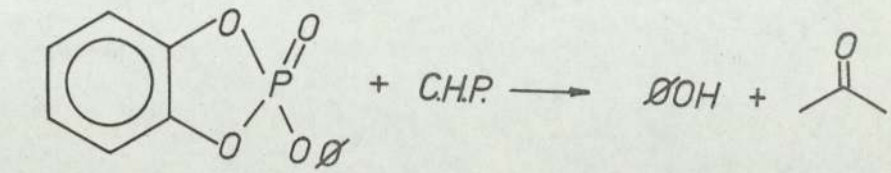
at 107°C

Fig VII

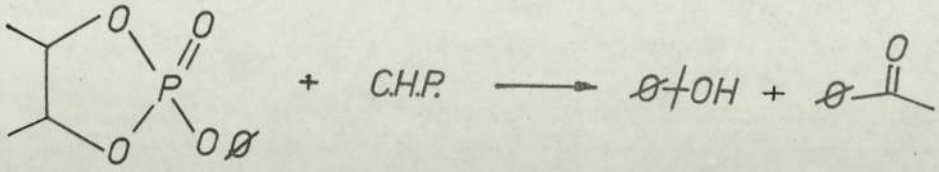


The decomposition of 2-t-butoxy-2-oxo-1,3,2-dioxaphospholane at 53°C

phenoxy-1,3,2-dioxaphospholane free radical hydroperoxide decomposition products are obtained. (24).

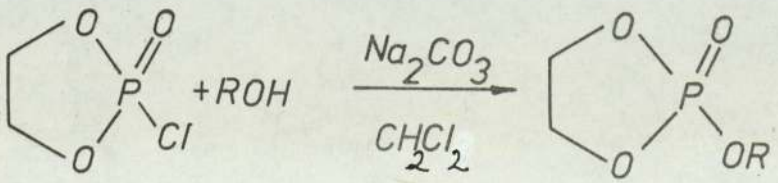


(24)



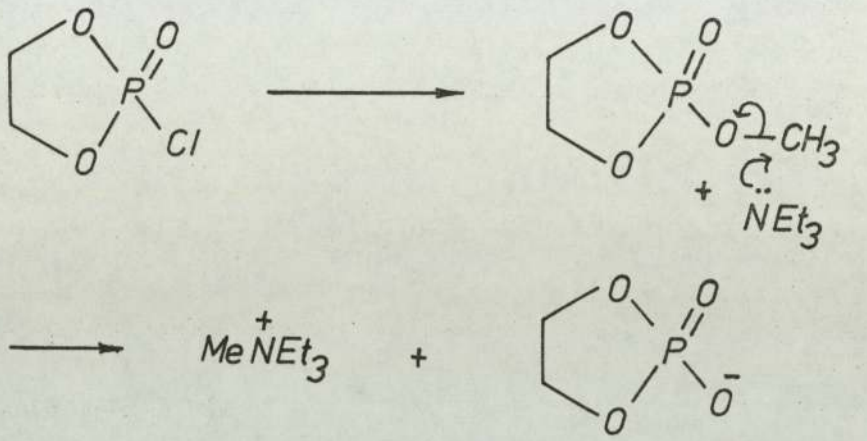
3.3 Aliphatic Alkyl Esters.

Many literature methods exist for the preparation of alkyl cyclic phosphates[53]. These methods include dinitrogen tetroxide oxidation[67], mercuric oxide oxidation[68], hydroperoxide oxidation, oxygen oxidation, and ozone oxidation of cyclic phosphites. However the phosphites concerned are toxic and unpleasant to handle, and so the preparations were attempted by the reaction of 2-chloro-2-oxo-1,3,2-dioxaphospholane with a suitable alcohol in methylene chloride in the presence of anhydrous sodium carbonate, (25) to absorb hydrogen chloride.



(25)

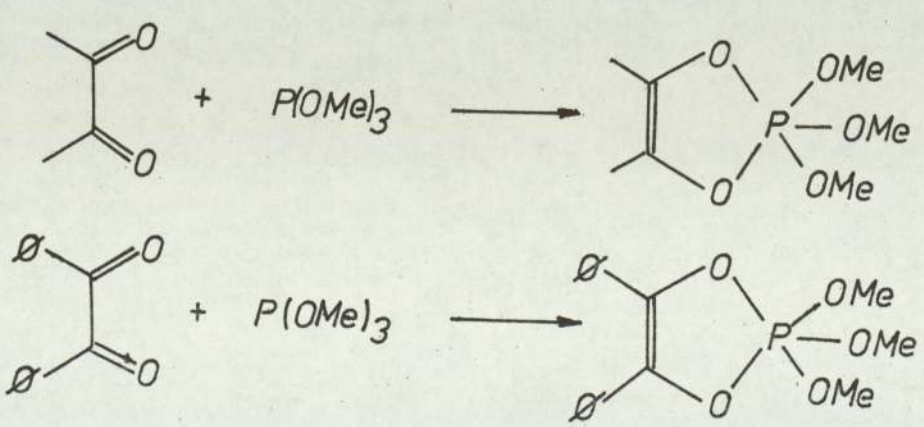
Yields of 80% and over were obtained for R = Me,Et, but the reaction did not give high yields for R = aryl. The use of a tertiary base to absorb hydrogen chloride was found to be unsuccessful as the quaternary salt was readily formed. (26).



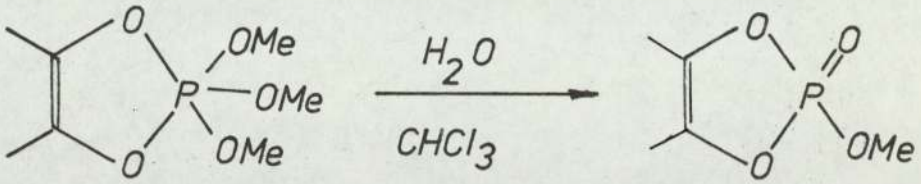
(26)

Mercuric oxide oxidation of the phosphites proved useful for the preparation of aromatic cyclic phosphates, as dinitrogen tetroxide gave nitroso derivatives and therefore low yields of the required cyclic phosphate esters.

In order to study the effect of a double bond on hydroperoxide decomposition 2.2.2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholane- $\triangle$4-ene was prepared; the 4,5-diphenyl analogue was also synthesized by the following routes (69),

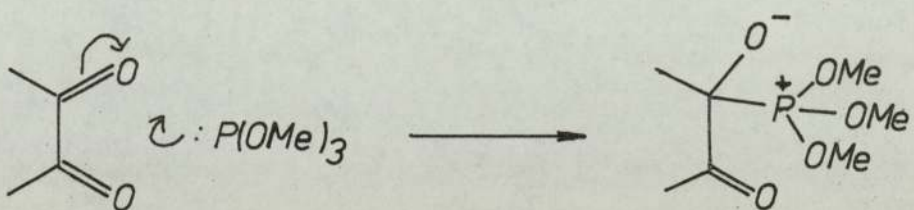


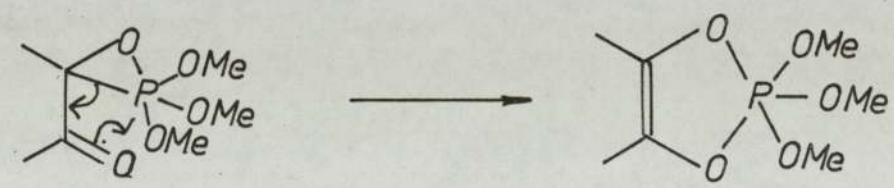
carefully controlled hydrolysis gave the cyclic phosphate ester. (27a)



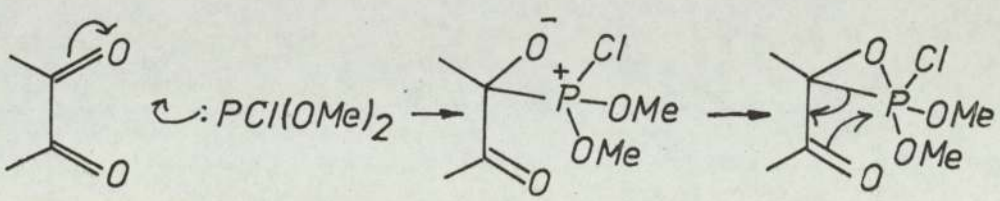
(27a)

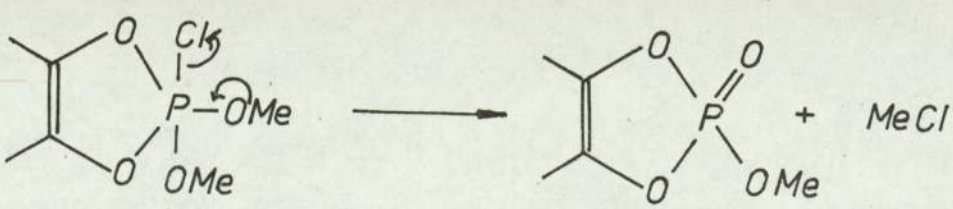
A better route to 2-methoxy-4,5-dimethyl-2-oxo-1,3,2-dioxaphospho-Δ^4-ene, proved to be the reaction of diacetyl with chlorodimethoxy phosphine[70]. The probable mechanisms of the reactions described are given below (27).





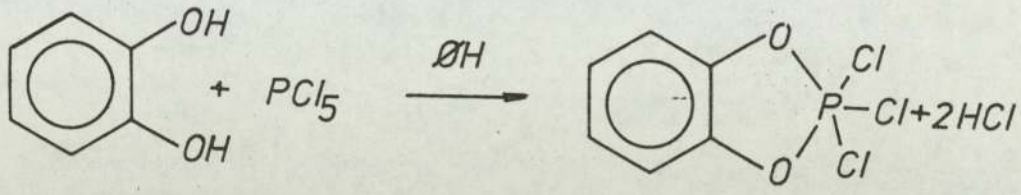
(27)



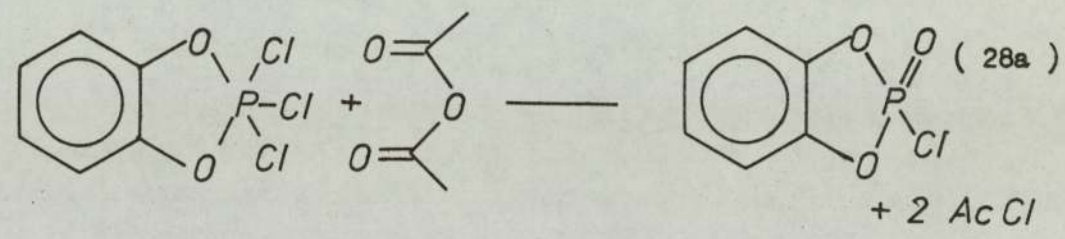


3.4 Aromatic cyclic phosphate esters.

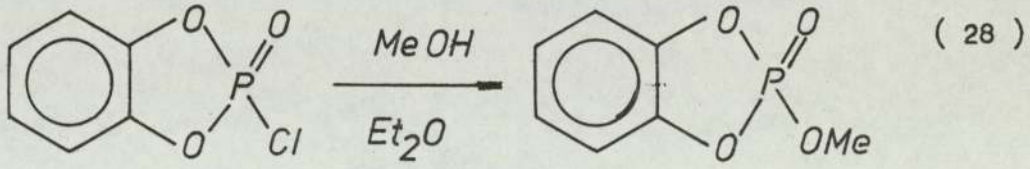
The synthesis of 2,2,2-trichloro-4,5-benzo-1,3,2-dioxaphospholane was attempted by a modification of that used by Anschütz (62).



The product was obtained in 80% yield and reacted with acetic anhydride to give 2-chloro-2-oxo-4,5-benzo-1,3,2-dioxaphospholane in 40% yield (28a).

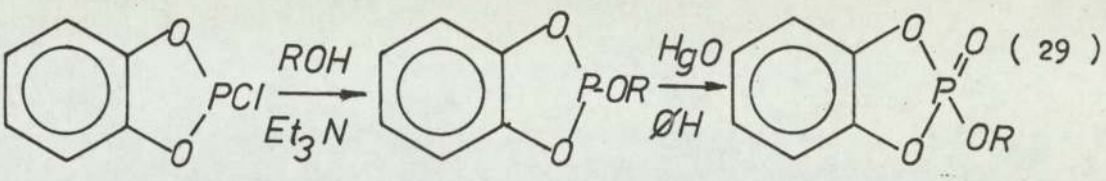


The reaction of methanol with 2-chloro-2-oxo-4,5-benzo-1,3,2-dioxaphospholane gave an almost quantitative yield of the corresponding methyl ester (28).



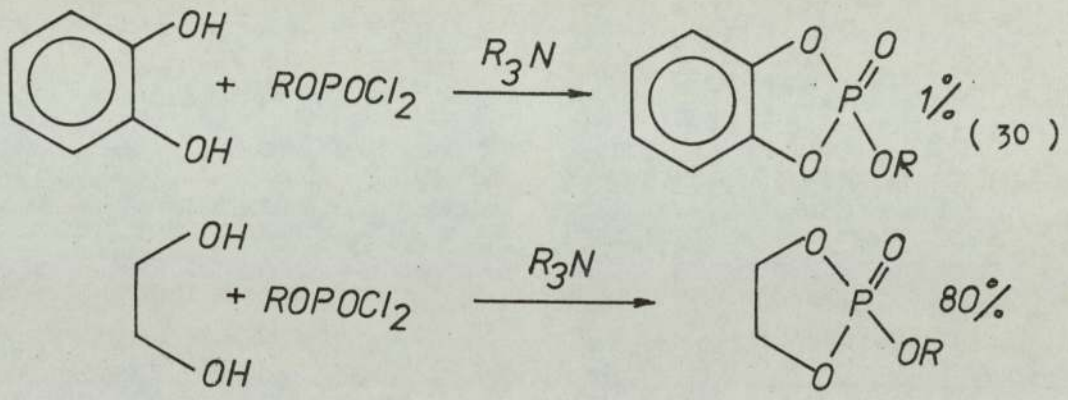
Other alcohols required the presence of a tertiary base to absorb hydrogen chloride. It was found that the oxidation of catechol phosphites with mercuric oxide in benzene provided another

convenient route for catechol phosphates. (29).



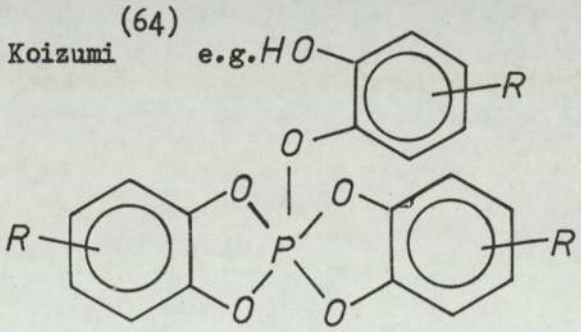
(29)

The reaction of aromatic diols with alkoxyphosphodichloridates in the presence of a tertiary amine did not prove to be a successful method for the preparation of catechol phosphates; this however works very well for aliphatic cyclic phosphates (30).

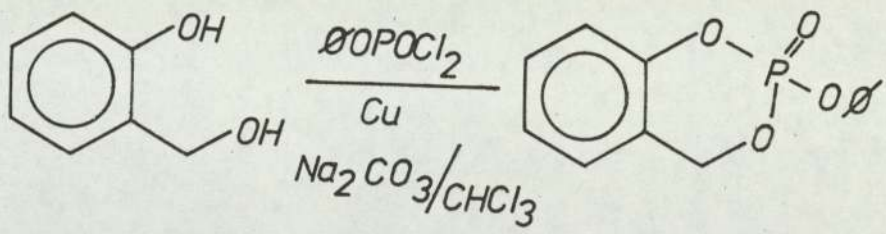


(30)

The products from the reaction of catechol and naphthalene diol with alkyl phosphodichloridate were similar in structure to those obtained by Koizumi[64] e.g.



The reaction of saligenin with phenyl phosphodichloridate in the presence of sodium carbonate and copper powder gave high yields of the required cyclic phosphate. (31).

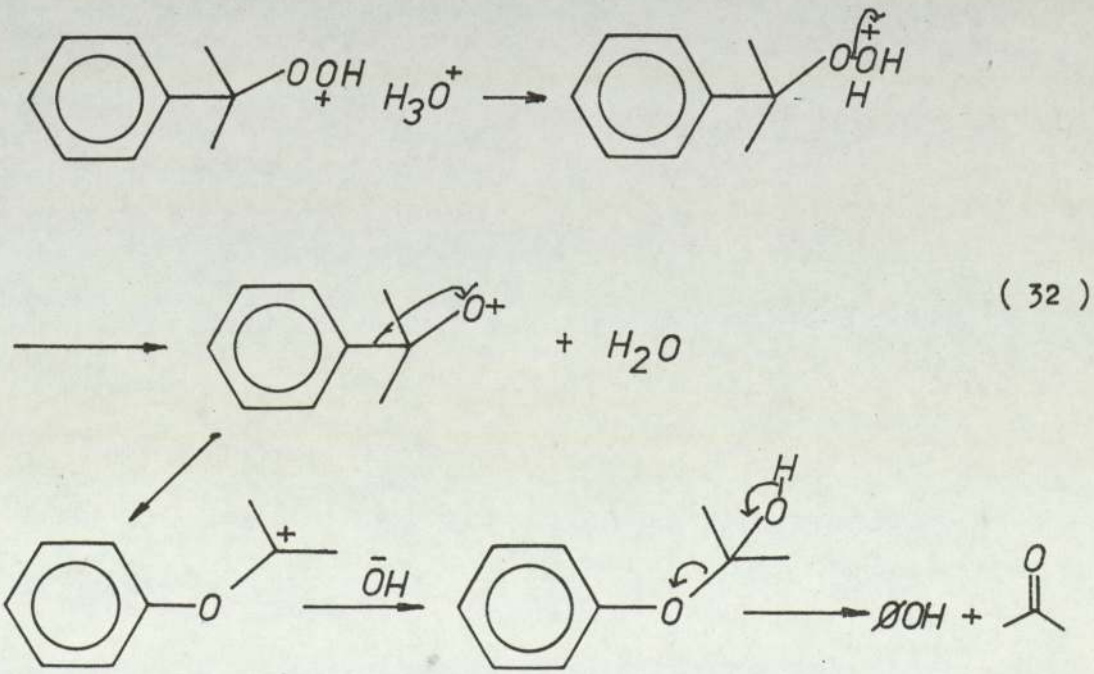


(31)

The copper probably acts as a template in the synthesis, and explains the high yield of product.

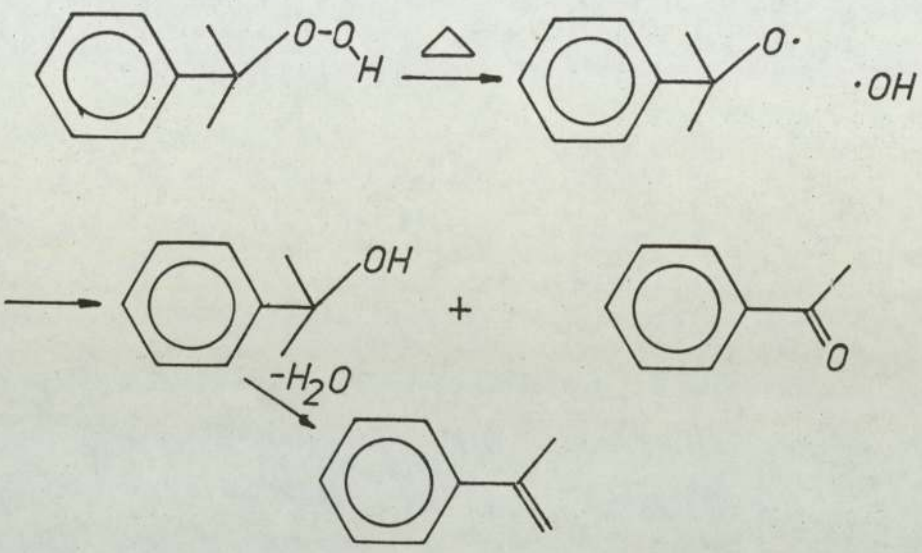
4.0 THE REACTIONS OF CYCLIC PHOSPHATE ESTERS WITH HYDROPEROXIDES

The reactions of a variety of cyclic phosphate esters with different hydroperoxides have been studied. The pure hydroperoxide (0.1mole/L.) was treated with the desired catalyst at 75°C., usually under nitrogen in the apparatus described in chapter 2. The reaction was followed by measuring the amount of unused hydroperoxide at set time intervals, by n.m.r. or an iodometric method. The analysis of hydroperoxide decomposition products was carried out by quantitative G.L.C. (see chapter 2). The hydroperoxide decomposition products can give an insight into the mechanism of the reaction[71], Lewis acids react with hydroperoxides to yield ionic products[72], thus for cumene hydroperoxide, acidification yields phenol and acetone (32).



(32)

The thermal decomposition of cumene hydroperoxide proceeds by homolysis of the peroxy bond, and certain transition metal ions can effect this type of decomposition (33).



(33)

Various other products can also be formed depending on the reaction conditions, thus when heated with animal charcoal, cumene hydroperoxide affords a high yield of dicumyl peroxide (73).

4.1. Aliphatic series.

Results

The reaction of bis-(2-oxo-1,3,2-dioxaphospholane)-2-oxide with cumene hydroperoxide was studied in chlorobenzene at a variety of concentrations and temperatures. Catalytic amounts (100 : 1) of the pyrophosphate did not appear to appreciably change the hydroperoxide concentration, in air or nitrgen, but a stoichiometric reaction was evident, and the decomposition of cumene hydroperoxide at higher pyrophosphate concentrations was measured.

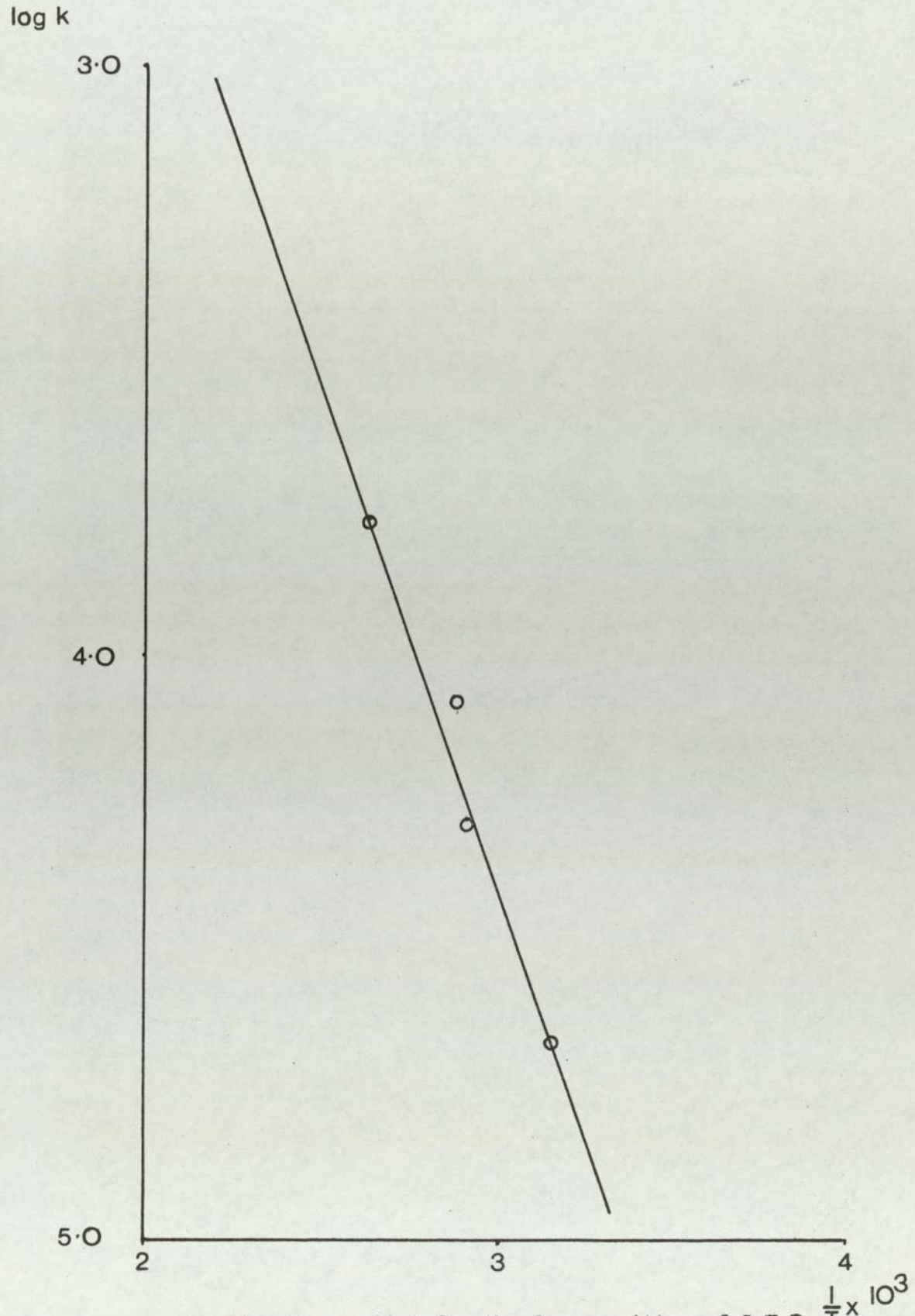
The reaction of two moles of hydroperoxide showed first order kinetics; the rate changed after one mole of hydroperoxide had been consumed, and a slower reaction followed. The rate of the slower reaction was comparable with that of the decomposition of cumene hydroperoxide using 2-hydroxy-2-oxo-1,3,2-dioxaphospholane, (see below). Table V shows the effect of temperature on rate constant for the first stage of the reaction between cumene hydroperoxide and bis-(2-oxo-1,3,2-dioxaphospholane)-2-oxide.

Table V

Temperature	CHP (pyrophos.)	rate const. sec^{-1}.
75	2	1.72×10^{-4}
60	2	9.39×10^{-5}
50	2	6.05×10^{-5}

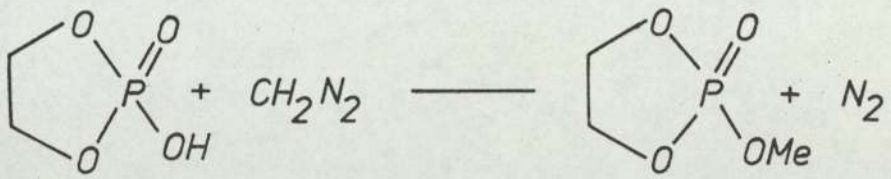
The rates of reaction did not change under nitrogen or air, and added 2,6-di-t-butyl-4-methylphenol did not affect the rate. The reproducibility was within ± 6%. In order to investigate the products of the decomposition of bis-(2-oxo-1,3,2-dioxaphospholane)-2-oxide with cumene hydroperoxide, a reaction carried out at 75°C. was cooled in an ice bath before completion. A detailed analysis of the phosphorus products showed that 2-hydroxy ethylphosphate, 2-hydroxy-2-oxo-1,3,2-dioxaphospholane, and a polymer were formed. The cyclic phosphate crystallized from the reaction mixture on

Fig VIII



Activation Energy Plot for the decomposition of C.H.P. (0.02 mole) with 2.5.9. (0.01 mole).

cooling, and was characterized by conversion to the methyl ester by means of diazomethane[74]. (34).



(34)

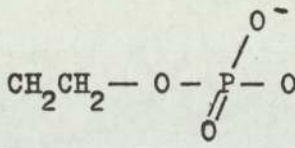
Activation energy calculation (Fig. VIII) gave a value of Ea = 10.1 K cal mol.$^{-1}$. The hydroperoxide decomposition products were shown to be acetone, phenol and α-methyl styrene with a trace of acetophenone (Table VI).

Table VI

	ØOH	acetone	α-me Styrene	Ø⌊OH	Ø⌊O	Temp. °C
mole%	36.7	32.7	50.1	2.8	-	75

The hydroperoxide decomposition products were determined after the reaction had gone to completion because cumene hydroperoxide was found to decompose on the G.L.C. column.

The reaction of 2-hydroxy-2-oxo-1,3,2-dioxaphospholane again showed first order kinetics; the phosphate was sparingly soluble in chlorobenzene, and the rate constants must be considered minimum values. At a 2 : 1 cumene hydroperoxide : phosphate ratio at 75 °C. the rate constant was found to be 2.69 x 10^{-5} sec.$^{-1}$, the reaction did not go to completion and product analysis showed the presence of polymeric material containing



units. The decomposition was inhibited by water. (see chapter 5).

4.1.1 Alkyl ester decomposition - Results.

The decomposition of cumene hydroperoxide with the methyl, isopropyl and phenyl esters of 2-hydroxy-2-oxo-1,3,2-dioxaphospholane was studied. Catalytic quantities of 2-methoxy-2-oxo-1,3,2-dioxaphospholane produced polymeric materials, and only at high concentrations of ester, were reactions observed.

The n.m.r. spectra of mixtures of 2-methoxy and 2-isopropoxy-2-oxo-1,3,2-dioxaphospholane with cumene hydroperoxide showed little change at room temperature over a period of several days (Fig. IX). At 75°C. reactions were observed with cumene hydroperoxide, and for 2-methoxy-2-oxo-1,3,2-dioxaphospholane at a 1 : 1 molar ratio $K_1 = 1.4 \times 10^{-5}$ sec.$^{-1}$. The rate for 2-isopropoxy-2-oxo-1,3,2-dioxaphospholane was much slower, due possibly to the bulky nature of the isopropyl group, preventing attack by hydroperoxy ion at phosphorus. (Table VII).

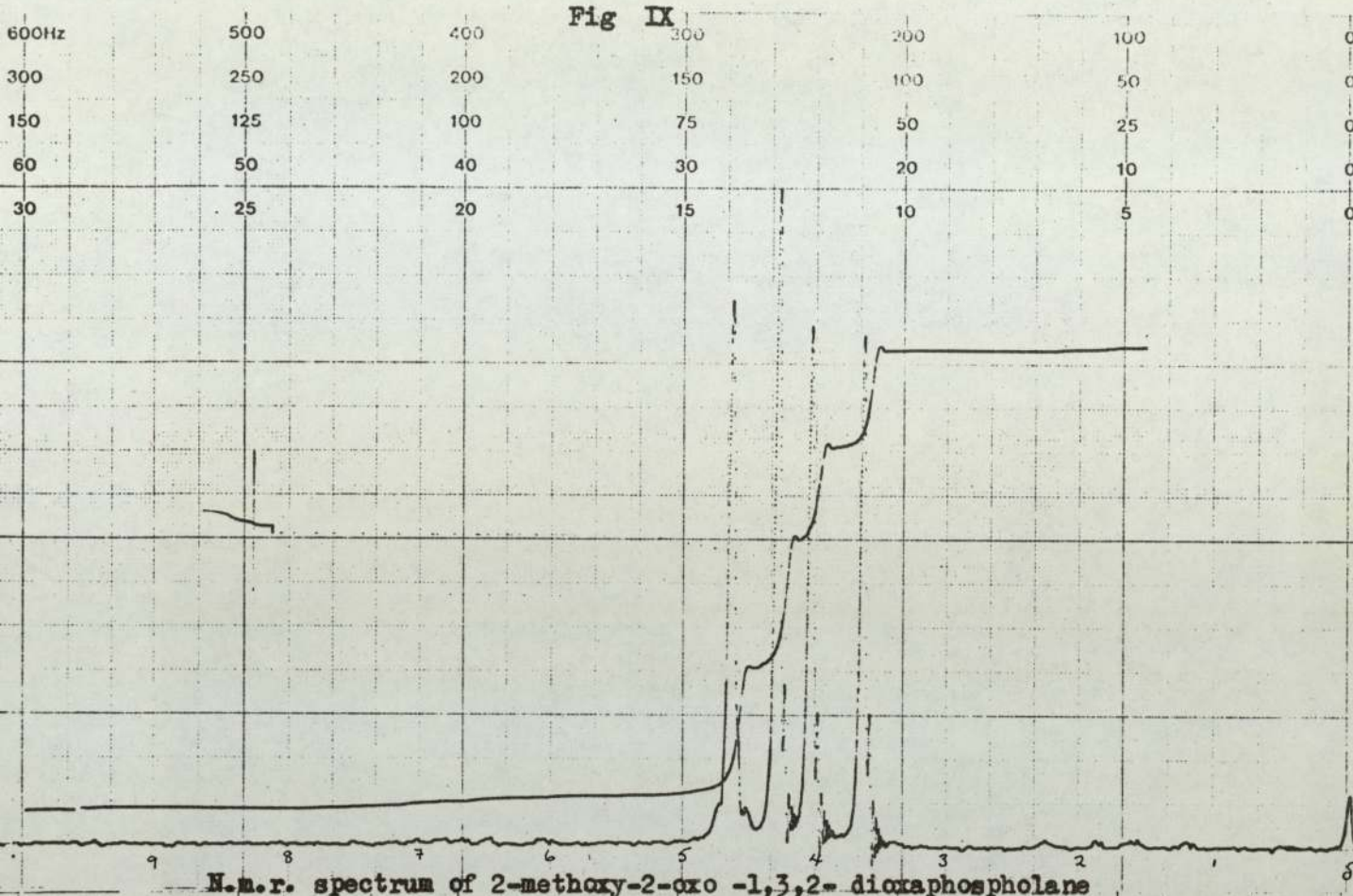
Table VII

Hydroperoxide distribution for the decomposition with 2- isopropoxy-2-oxo-1,3,2-dioxaphospholane in chlorobenzene at 75°C.

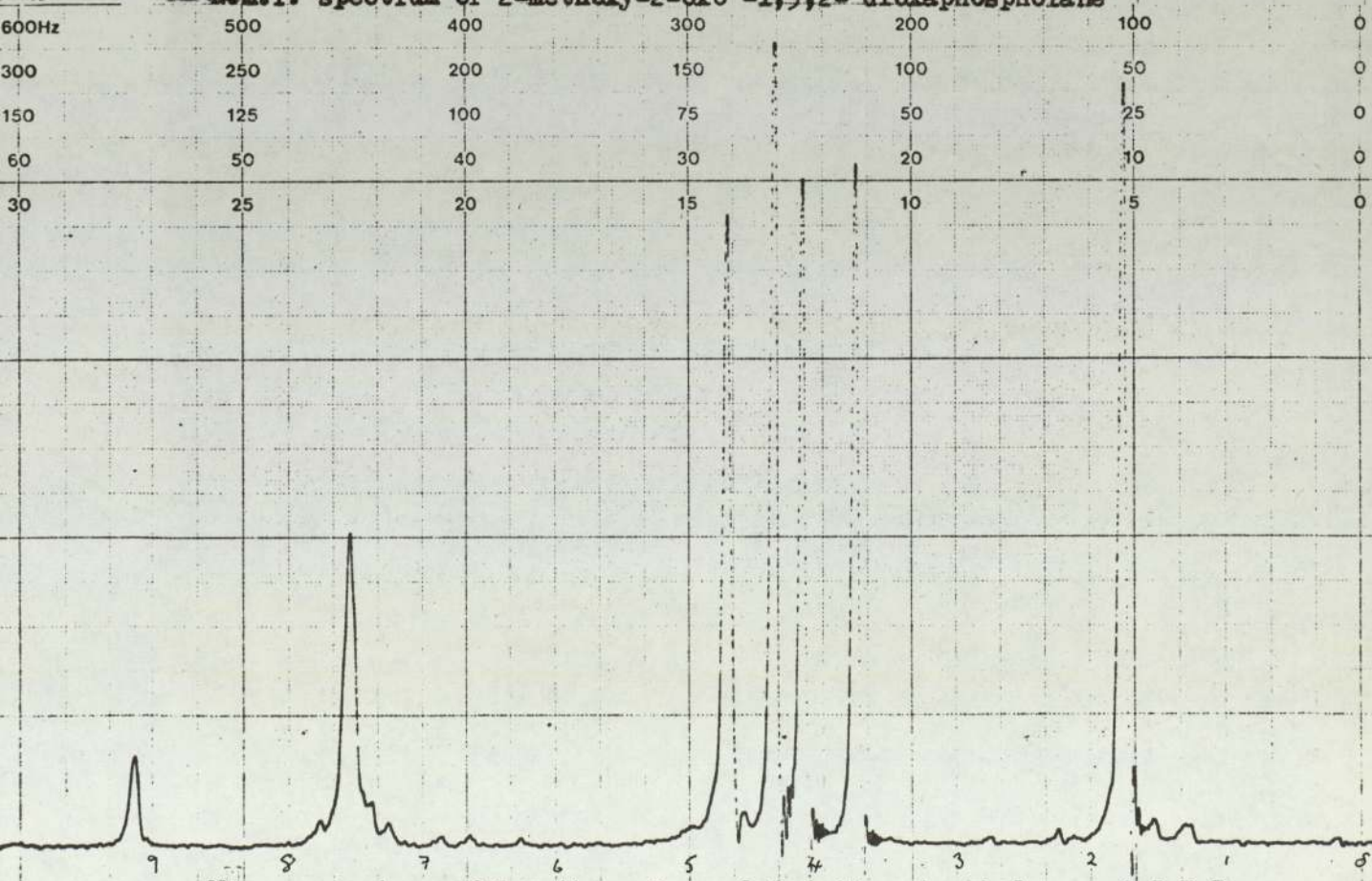
						$\frac{[CHP]}{[phosphate]}$	Temp.
mole%	76.2	27.7	37.5	5.27	0.2	1	75°C.

Isopropanol was detected in the reaction mixture.

Fig IX



N.m.r. spectrum of 2-methoxy-2-oxo -1,3,2- dioxaphospholane



N.m.r. spectrum of 2-methoxy-2-oxo-1,3,2-dioxaphospholane and C.H.P.

showing no apparent decomposition.

The methyl, isopropyl and tertiary butyl esters of pinacol cyclic phosphate showed no effect on the decomposition of cumene hydroperoxide even after 48 hr. using stoichiometric quantities. T.L.C. showed unchanged pinacol cyclic ester, after this period of time.

The phenyl ester of 2-hydroxy-2-oxo-1,3,2-dioxaphospholane was shown to be more effective as a peroxide decomposer than either the methyl or isopropyl esters. Catalytic quantities of greater than 100 : 1 did not react, but 10 : 1 quantities showed an initial reaction which ceased after 1.5 to two moles of hydroperoxide had been consumed. The reactions were not first order at 10 : 1 ratios. It was found that stepwise replacement of the hydrogen atoms in the dioxaphospholane ring reduced the rate of decomposition, but did not destroy the ability of the phosphate to destroy up to two moles of hydroperoxide.

Table VIII

Rate constants for the stoichiometric reaction of phenyl phosphates using cumene hydroperoxide plotted as first order.

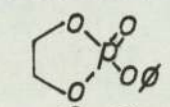
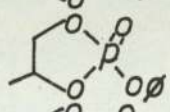
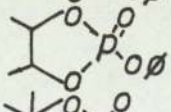
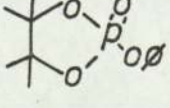
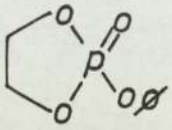
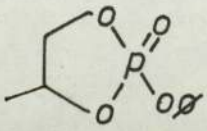
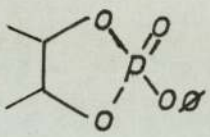
Compound	Rate constant sec.$^{-1}$	Temp. °C.	$\frac{[CHP]}{[phosphate]}$
	7.46×10^{-5}	75	1
	3.79×10^{-5}	75	1
	1.1×10^{-5}	75	1
	-	75	1

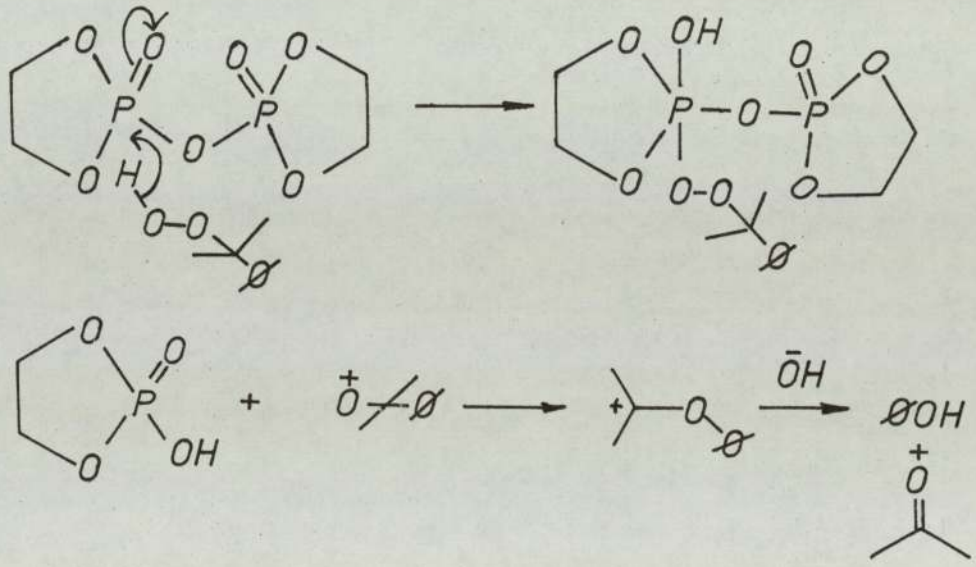
Table IX

Hydroperoxide product analysis.

Compound	% product distribution					Temp. °C
	ØOH	O<	Ø<	Ø<OH	Ø<O	
	62.8	11.3	24.2	1.6	-	75
	52.25	1.17	43.4	3.13	-	75
	42.8	neg.	16.11	8.2	32.4	75

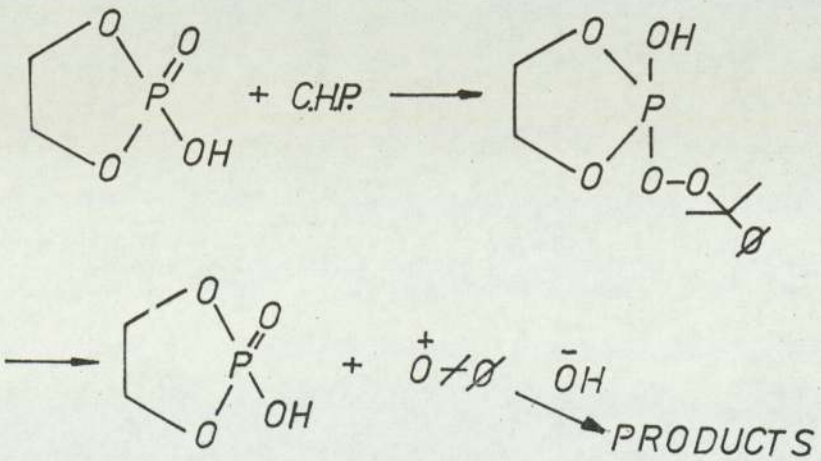
4.2 The aliphatic series :- discussion.

Bis-(2-oxo-1,3,2-dioxaphospholane)-2-oxide appears to react with cumene hydroperoxide by an ionic mechanism; the rate of reaction was not affected by the addition of the radical trapping species 2,6-di-t-butyl-4-methylphenol, or by reactions carried out in dry air or nitrogen. The reaction appears to take place in three stages (see chapter 6 for a discussion of the first stage). The second stage involves a first order decomposition possibly due to the destruction of the pyrophosphate as follows. (35).



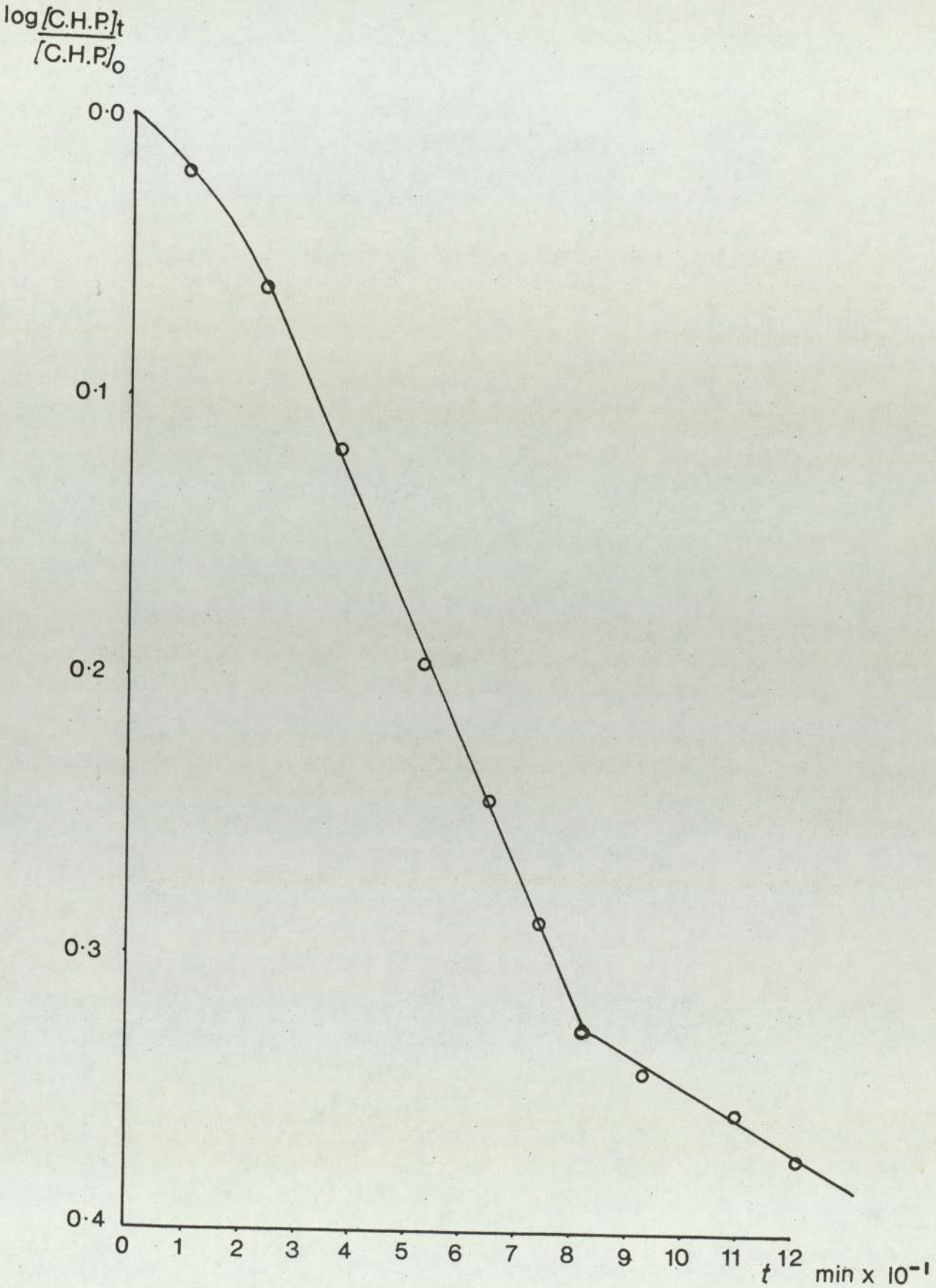
(35)

The third stage is slower and may involve reaction of hydroperoxide with 2-hydroxy-2-oxo-1,3,2-dioxaphospholane. (36).



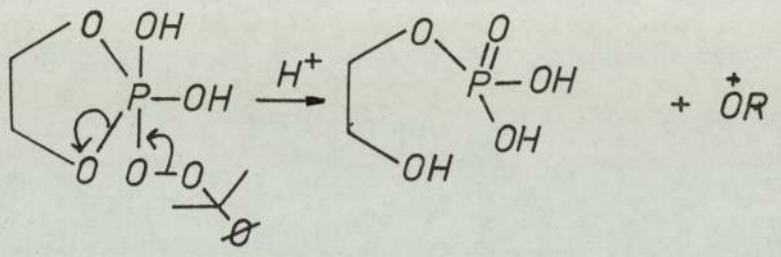
(36)

Fig X



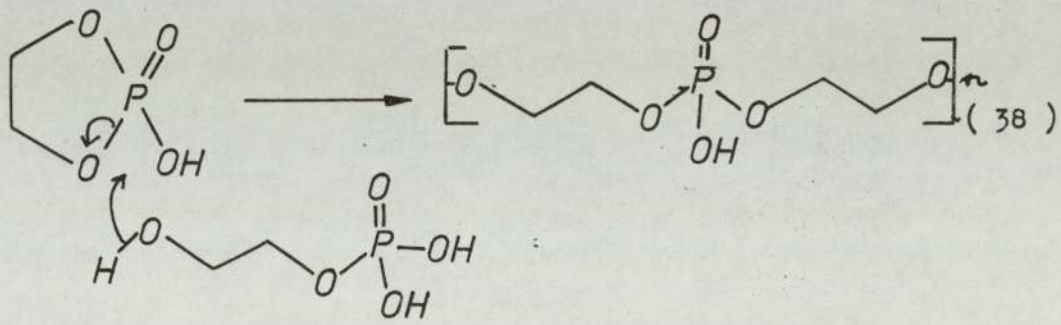
The decomposition of C.H.P. (0.02 mole) with 2.5.9. (0.01 mole) at 75°C

The reaction product analysis supports the previous mechanisms. Scheme (36) depicts the situation for a catalytic reaction, which was not observed in the above case. The transition state involves a pentavalent complex void of ring strain[75], and formation of the cyclic phosphate involves the conversion to a strained system, thus it should be more favourable for ring opening as shown below. (37).



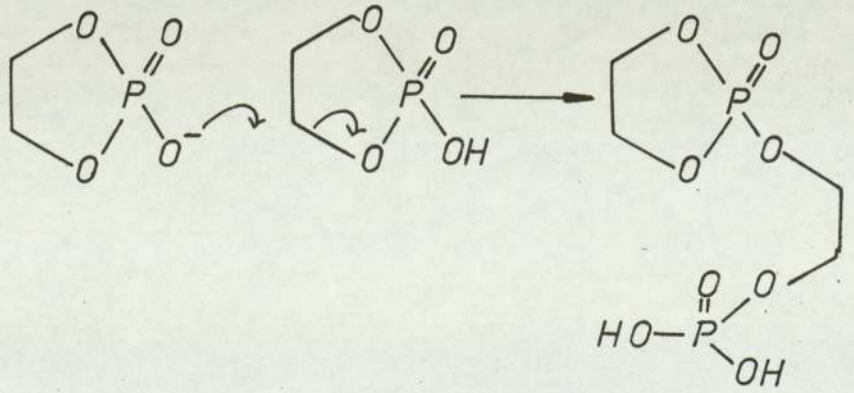
(37)

2-Hydroxyethyl phosphate was shown to be a reaction product. Polymeric material was obtained, and this can be explained by the attack of hydroxyl ion on a cyclic unit, (38),



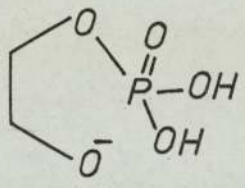
(38)

alternatively attack of phosphate anion on carbon is possible. (39)

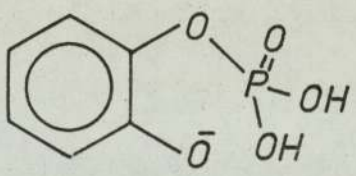


(39)

The relief of ring strain at the transition state, and also the ease of polymerisation of these compounds, may explain why they do not possess the catalytic activity associated with the catechol phosphates[14][15][16] (see chapter 5.0). The other fundamental difference is the lack of a suitable electron withdrawing group to delocalize the negative charge formed on the oxaphospholane oxygen ;



a



b

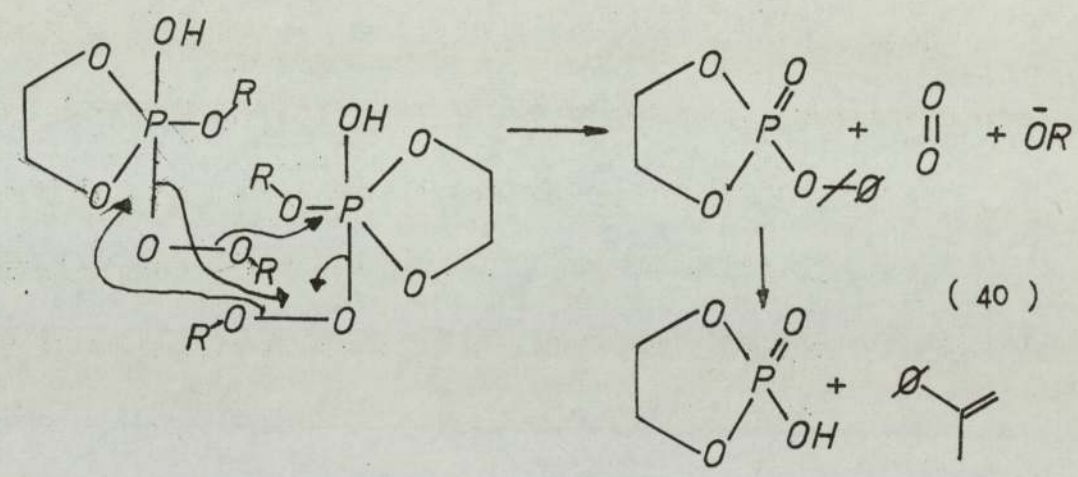
in case a delocalization is not possible, but in b the possibility exists, and a quasi aromatic transition state may be obtained as the carbon atom neighbouring the oxanion is sp^2 hybridized. With this idea in mind cyclic phosphate esters containing double bonds were synthesized, and reacted with various hydroperoxides, the results of these reactions are discussed in the next chapter.

The methyl and isopropyl esters of 2-hydroxy-2-oxo-1,3,2-dioxaphospholane were found to react similarly to bis(2-oxo-1,3,2-dioxaphospholane)-2-oxide, and the hydroperoxide decomposition products were found to be phenol and acetone, together with appreciable quantities of α-methyl styrene, but only traces of

acetophenone.

The origin of ∝ methyl styrene in these reactions was at first not clear; homolysis of the peroxide bond in the transition state would lead to cumyloxy radicals, which could then abstract hydrogen atoms to form cumyl alcohol, followed by dehydration of cumyl alcohol forming ∝-methyl styrene[76].

A mechanism consistent with the ionic nature of the reactions could involve a cyclic six membered transition state (40).

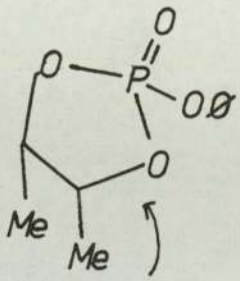


(40)

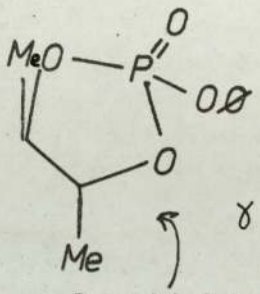
However oxygen evolution was not observed and no products arising from singlet oxygen-solvent interactions were observed. The above mechanism proved to be sterically unsound. An eight membered cyclic mechanism[77] is possible, and may be more important for the aromatic cyclic esters (see chapter 5). The most likely source of ∝ methyl styrene, consistent with an ionic mechanism, is from dicumyl peroxide; these reactions are discussed fully in the next chapter.

The decomposition of cumene hydroperoxide using the phenyl

esters of Table VIII, shows that increasing the number of methyl groups in the dioxaphospholane ring slows the reaction down. Attempts to correlate rate with the number of methyl groups, show that the stereoisomers of the cyclic phosphates must be considered. The cis dimethyl-1,3,2-dioxaphospholane presents more steric hinderance than the trans (ɣ) for attack at phosphorus by

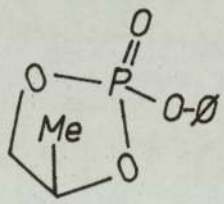


more hindered

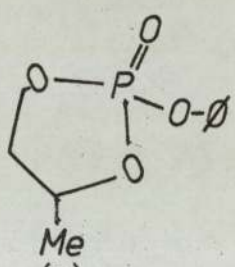


less hindered

hydroperoxide. In the case of the isomeric mixture of 4-methyl-2-phenoxy-1,3,2-dioxaphospholane,



(c)

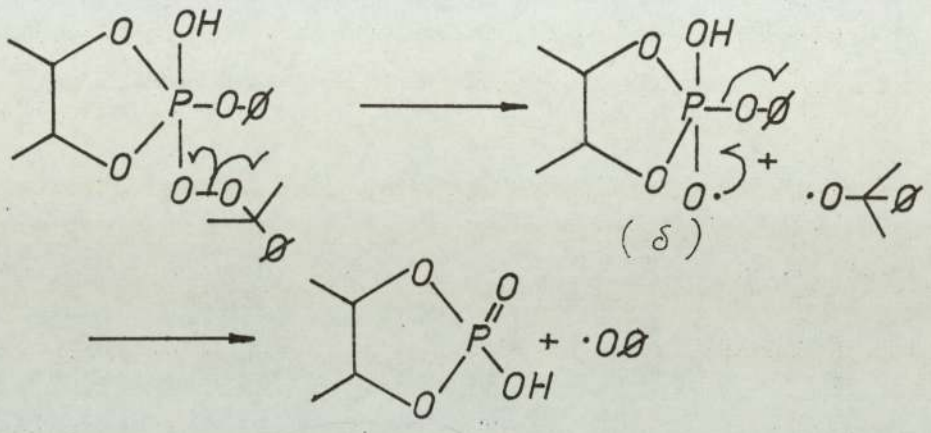


(d)

c should react faster than d. The ratios of isomers c and d can be calculated from the n.m.r. spectra (39). The rate factor for the addition of methyl groups is approximately 1.5. (see Table VIII).

The products of cumene hydroperoxide decomposition using the phenyl phosphates are interesting. 4,5-Dimethyl-2-phenoxy-2-oxo-1,3,2-dioxaphospholane shows a large proportion of cumyl

alcohol compared with the other phenyl esters. No acetone was produced, and when 2,6-di-t-butyl-4-methyl phenol was added to the reaction mixture, α-methyl styrene and phenol were the sole products. This supports a radical mechanism (41).



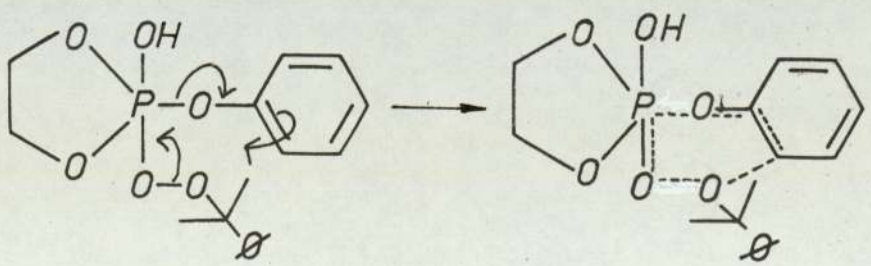
(41)

(δ)

(42)

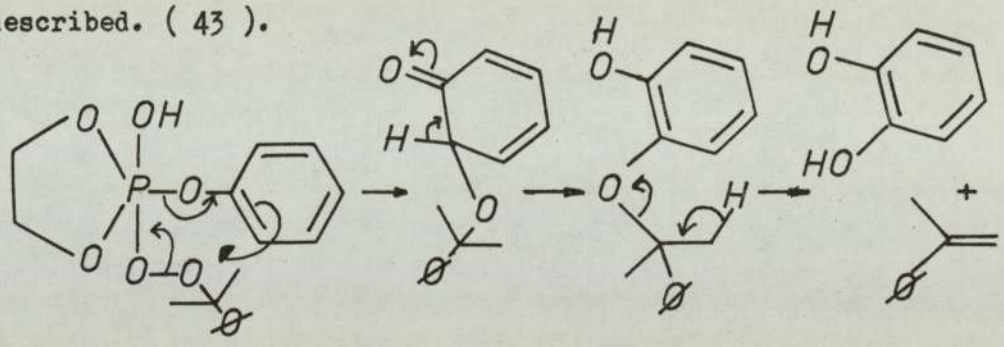
The intermediate radical (δ) has been shown to exist for pinacol derivatives. Thus increasing the number of methyl groups in the dioxaphospholane ring, increases the radical nature of the mechanism.

The enhanced rate of the decomposition of cumene hydroperoxide using 2-phenoxy-2-oxo-1,3,2-dioxaphospholane, and the ability to decompose an excess of one mole of hydroperoxide could be due to stabilization of the transition state as follows (42),



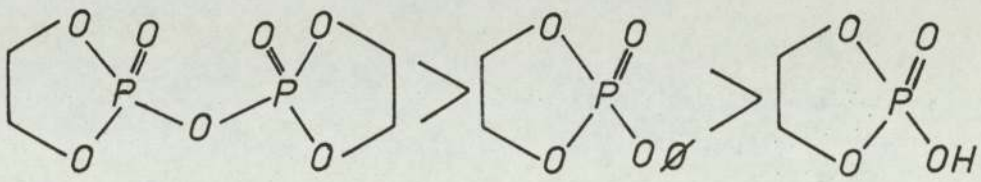
(42)

e.g. formation of an aromatic transition state ring opening followed by polymerization, however when the competing radical reaction removes the phenoxy group, the catalytic peroxide decomposing effect is destroyed; hence although these compounds are more powerful peroxide decomposers than the alkyl derivatives, they are not effective catalysts for the decomposition of hydroperoxide. Traces of catechol were found in the reaction mixture by T.L.C., and mass spectrometry, this supports the transition state previously described. (43).

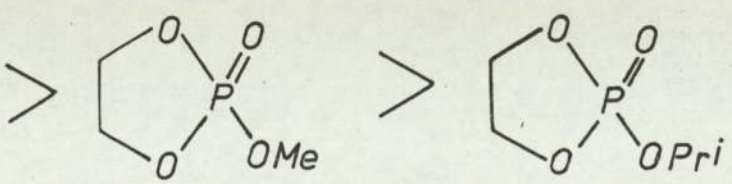


(43)

The order of reactivities of the aliphatic cyclic phosphates toward cumene hydroperoxide are as follows. (44).



(44)



5.0 THE REACTIONS OF AROMATIC CYCLIC PHOSPHATES WITH HYDROPEROXIDES

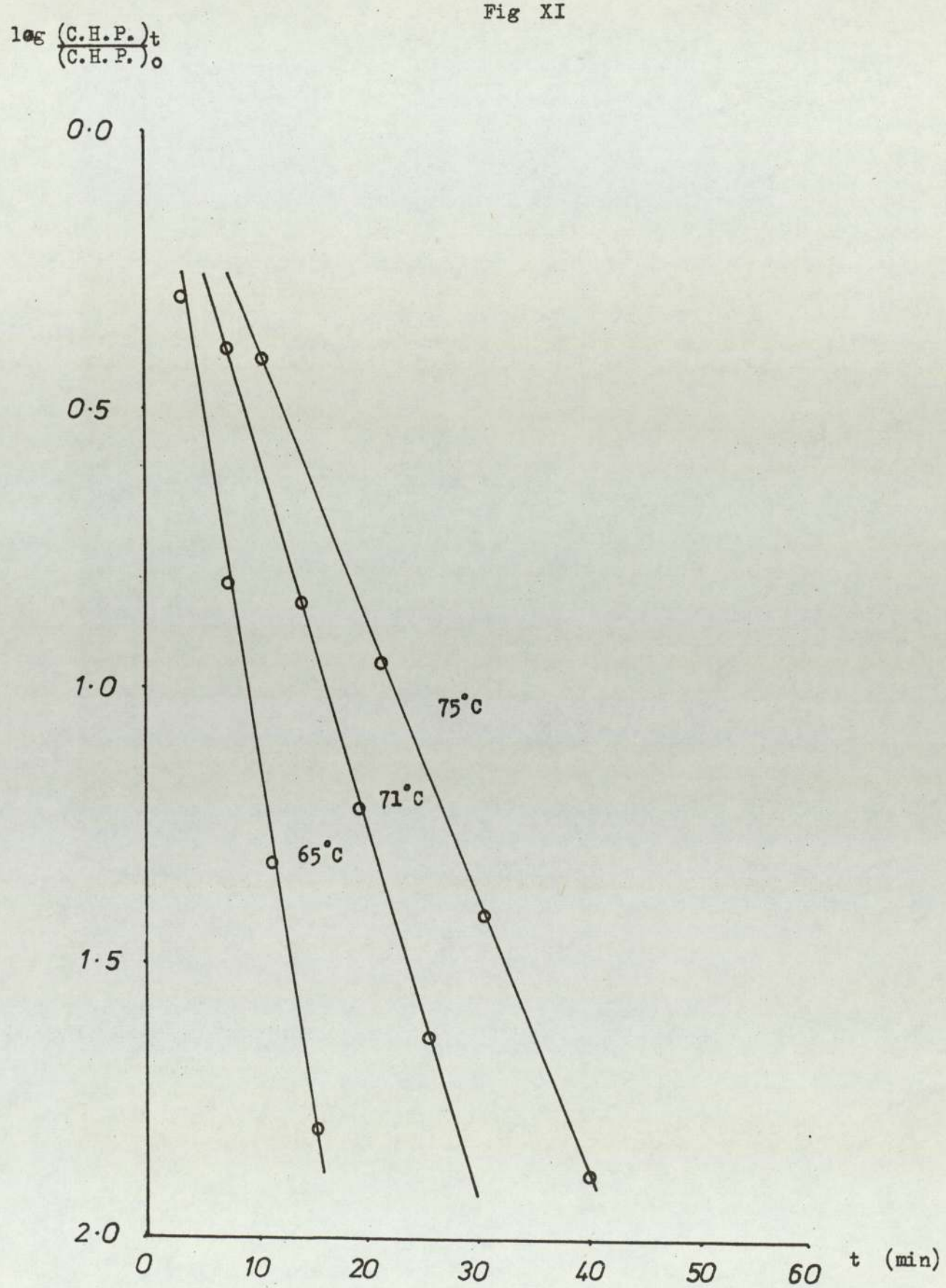
In contrast to the aliphatic series, the aromatic cyclic phosphates based on catechol are very powerful catalysts for the decomposition of hydroperoxide. Work has already been done on 2-(2,6-di-t-butylphenoxy)-2-oxo-4,5-benzo-1,3,2-dioxaphospholane (16), and on 2-hydroxy-2-oxo-4,5-benzo-1,3,2-dioxaphospholane, but no work has been done on the simple alkyl esters. A series of catechol cyclic phosphate esters were prepared, and found to be extremely hygroscopic materials, readily soluble in most organic solvents. The decomposition reactions of cumene hydroperoxide, ethylbenzene hydroperoxide, t-butyl hydroperoxide and dicumyl peroxide were studied in a variety of solvents and temperatures, using different concentrations of cyclic ester.

5.1 Results.

The decomposition of cumene hydroperoxide was studied in chlorobenzene in the presence of 2-methoxy-2-oxo-4,5-benzo-1,3,2-dioxaphospholane, at a variety of temperatures, in air or nitrogen, and in the presence of radical traps. Under these conditions no alteration in rate was noted. The kinetic results for a catalytic reaction using a 10 : 1 mole ratio of hydroperoxide to cyclic phosphate are summarized in Table X.

First order kinetics were observed, but it was shown that

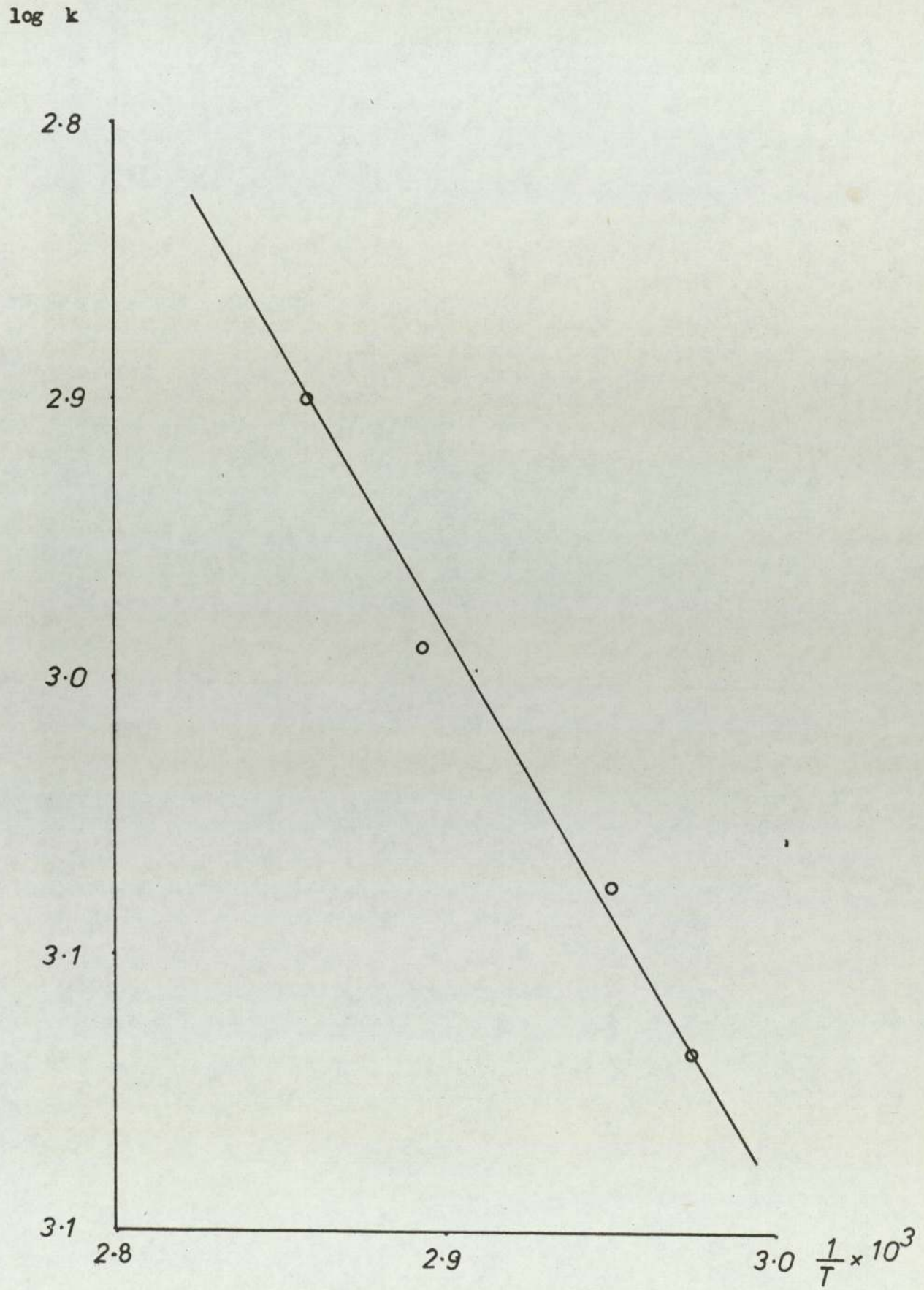
Fig XI



The decomposition of C.H.P. (0.1 mole) at various temperatures using 2.6.4.* (0.01 mole)

* see appendix

Fig XII



Activation Energy Plot for the decomposition of C H.P. (0.1 mole)

using 2.6.4.(0.01 mole)

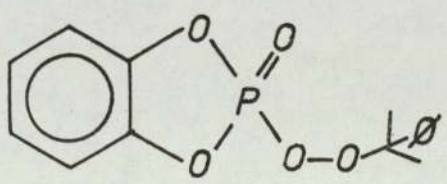
the rate constant was dependent on initial phosphate concentration, and thus a pseudo first order reaction of the type

$$-\frac{dc}{dt} = K(c)^1 (\text{phosphate})^x$$

was operating.

c = hydroperoxide concentration.

The phosphate concentration must be in a large excess, or not be destroyed in the reaction. The phosphate reaction products were o-hydroxy phenylphosphate, catechol cyclic phosphate, o-benzoquinone, and traces of methyl-o-hydroxy phenylphosphate. An n.m.r. study of this reaction was done in carbon tetrachloride. This reaction was faster than expected (solvent effect) and a singlet appeared at τ 8.65 which disappeared at the end of the reaction; this indicated a transient species. The methyl doublet did not disappear at this stage, indicating that the methyl group is not lost in the formation of the catalytic species, i.e. a phosphorus peroxide such as I is not formed (see appendix).



I

In view of the rate enhancement during the n.m.r. experiment, the kinetics of cumene hydroperoxide decomposition were investigated

in various solvents. A rate enhancement was noted in nitrobenzene; in cumene and chlorobenzene the rates were comparable.

Table X

Rate constants for the reaction of 0.1 M cumene hydroperoxide with 0.01 M. 2-methoxy-2-oxo-4,5-benzo-1,3,2-dioxaphospholane. (2.6.4.)

rate constant sec^{-1}	Temperature °C	Solvent
2.76×10^{-3}	75	ØCl
2.13×10^{-3}	71	ØCl
1.68×10^{-3}	65	ØCl

Table XI shows the hydroperoxide product distribution in chlorobenzene and cumene at a variety of temperatures using 2-methoxy-2-oxo-4,5-benzo-1,3,2-dioxaphospholane. (2.6.4).

Table XI

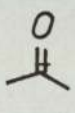
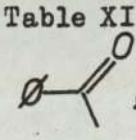
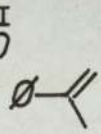
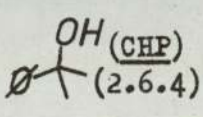
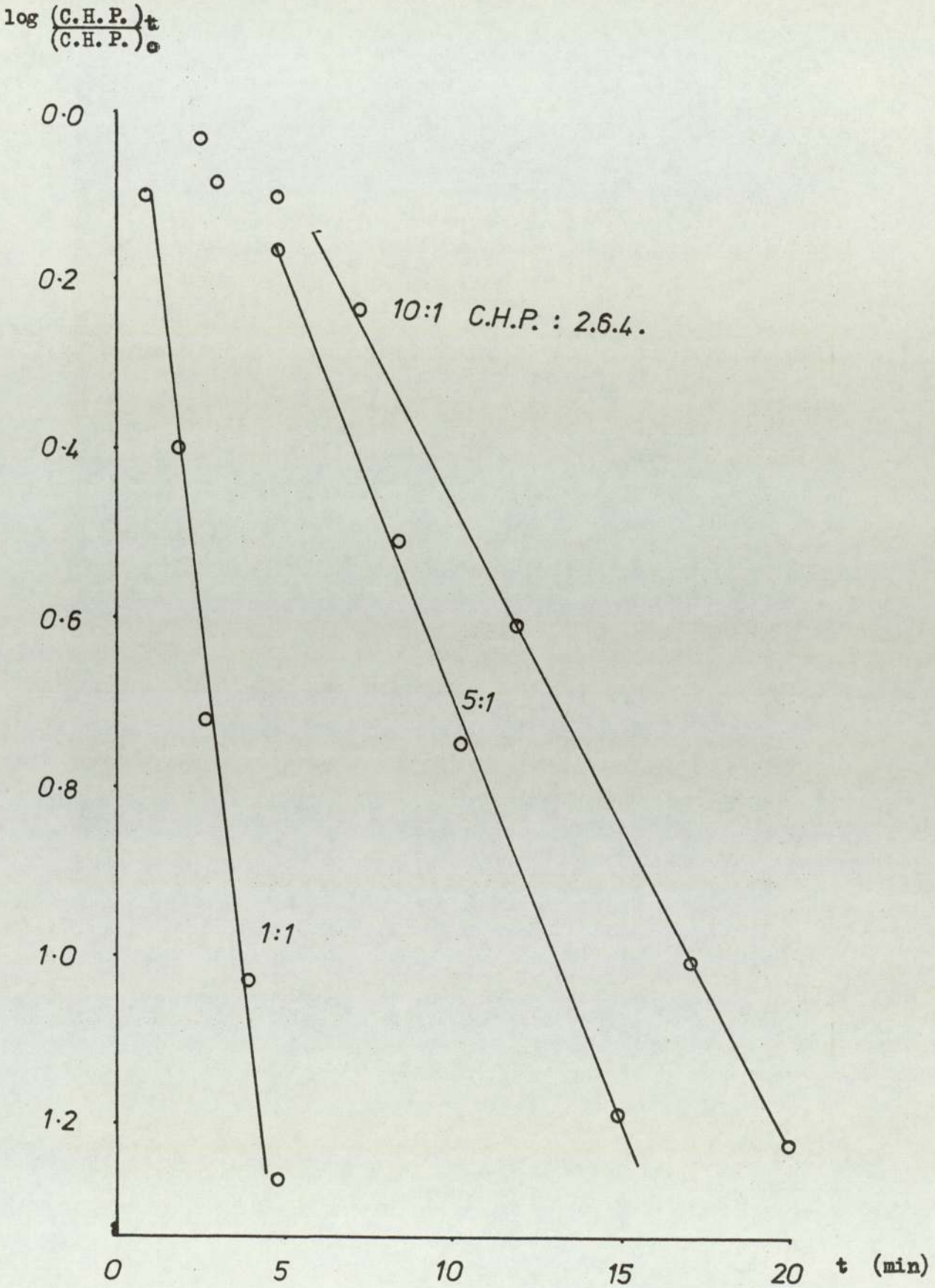
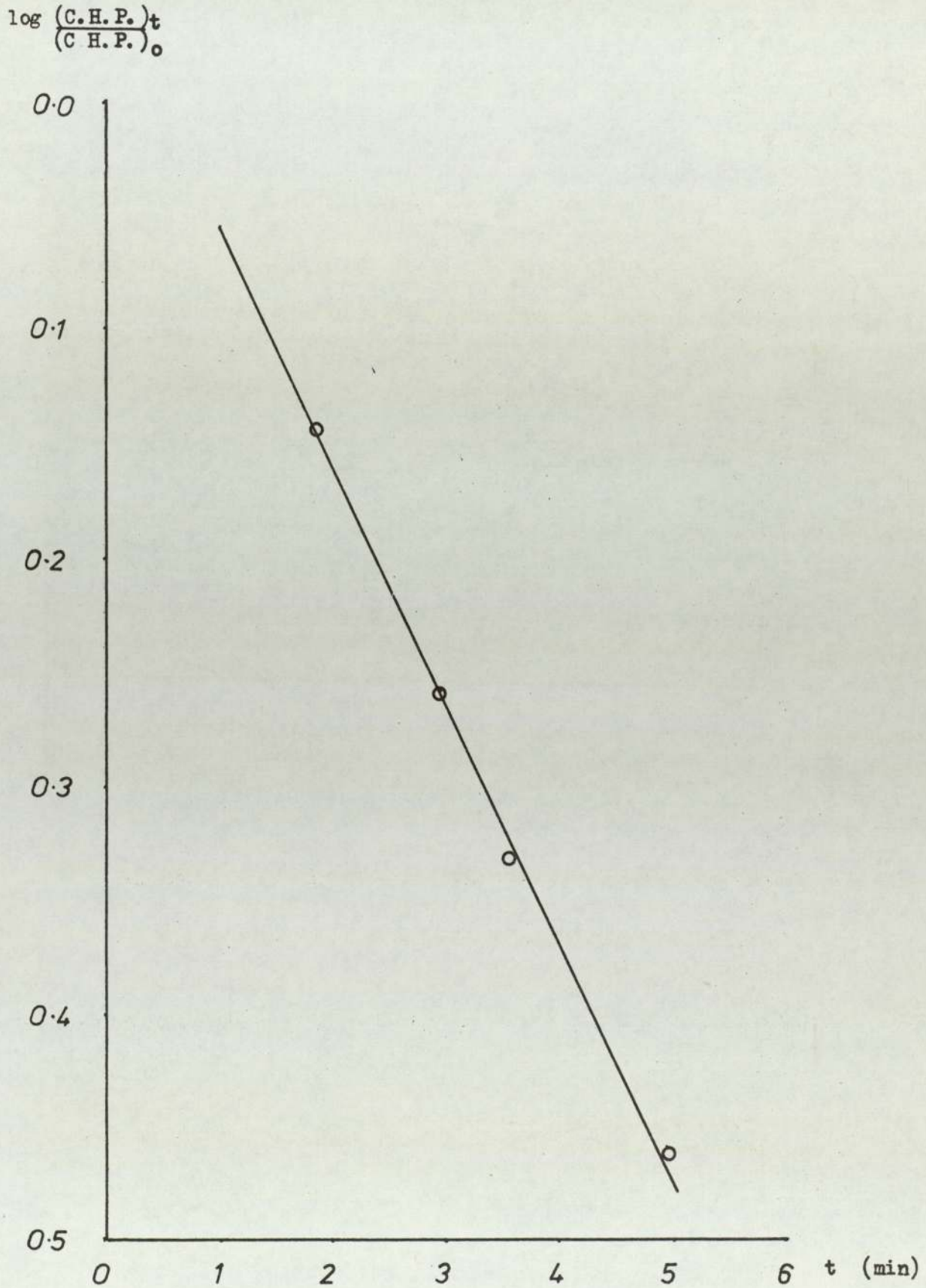
Temp. °C	ØOH				 (CHP) (2.6.4)		Solvent
75	72.1	65.4	14.7	1.5	-	10	ØCl
65	88.4	74.8	10.1	-	-	10	ØCl
55	90.2	72.0	9.2	-	-	10	ØCl
75	88.7	63.4	26.7	-	12.1	10	cumene

Fig XIII



Decomposition of C H.P. (0 1 mole) using various ratios of 2.6.4. in cumene at 75°C

Fig XIV



The decomposition of C.H.P. (0.1 mole) in ϕNO_2 using 2.6.4. (0.01 mole) at 75°C

Table XII

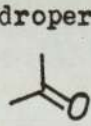
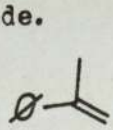
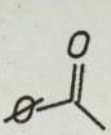
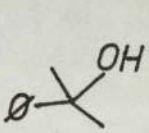
Decomposition of cumene hydroperoxide (0.1 M.) using different ratios of 2.6.4 in cumene and nitrobenzene.

Rate constant sec^{-1}	Temperature °C.	$\frac{(CHP)}{(2.6.4)}$	Solvent
3.49×10^{-3}	75	10	ϕPr^i
4.6×10^{-3}	75	5	ϕPr^i
9.57×10^{-3}	75	1	ϕPr^i
6.44×10^{-3}	75	10	ϕNO_2

Experiment showed that higher concentrations of catalyst led to the formation of more α methyl styrene (Table XIII), also less α-methyl styrene appears to be formed at lower temperatures

Table XIII

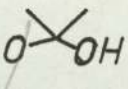
Product distribution in chlorobenzene at different concentrations of 2.6.4 using 0.1 M. cumene hydroperoxide.

Temp. °C	$\frac{(CHP)}{(2.6.4)}$	ØOH				
70	1	72.1	26.7	41.4	3.3	-
70	2	79.8	49.8	33.2	2.2	-
70	100	83	56	18.3	3.7	2.2

under catalytic conditions. The same trends were noted in cumene (Table XIV).

Table XIV

Product distribution in cumene at different concentrations of 2.6.4 using 0.1 M. cumene hydroperoxide.

Temp. °C.	$\frac{(CHP)}{(2.6.4)}$	ØOH				
75	10	88.7	63.4	26.7	-	12.1
75	5	80.6	49.0	30.1	-	
75	1	59.7	31.4	50.1	2.2	1.26

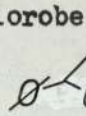
In each case less acetone appears in the mass balance, the losses cannot only be due to evaporation.

5.1.1 Reaction of 2.6.4 with ethylbenzene hydroperoxide (E.B.H.P.)

The kinetics of E.B.H.P. decomposition with 2.6.4 were followed. The product distribution for the reaction involving 0.1 M. E.B.H.P. is shown in Table XV.

Table XV

Product distribution for the decomposition of 0.1 M. E.B.H.P. using 0.01 M. 2.6.4 in chlorobenzene.

Temp.	$\frac{(EBHP)}{(2.6.4)}$	ØOH		aceto-phenone	Styrene	acet-aldehyde
75°C.	10	78.8	3.7	7.5	-	38.6

Lower concentrations of acetaldehyde than expected were found, this is almost certainly due to volatalization, as a cardice trap

connected to the kinetic apparatus collected considerable quantities of acetaldehyde.

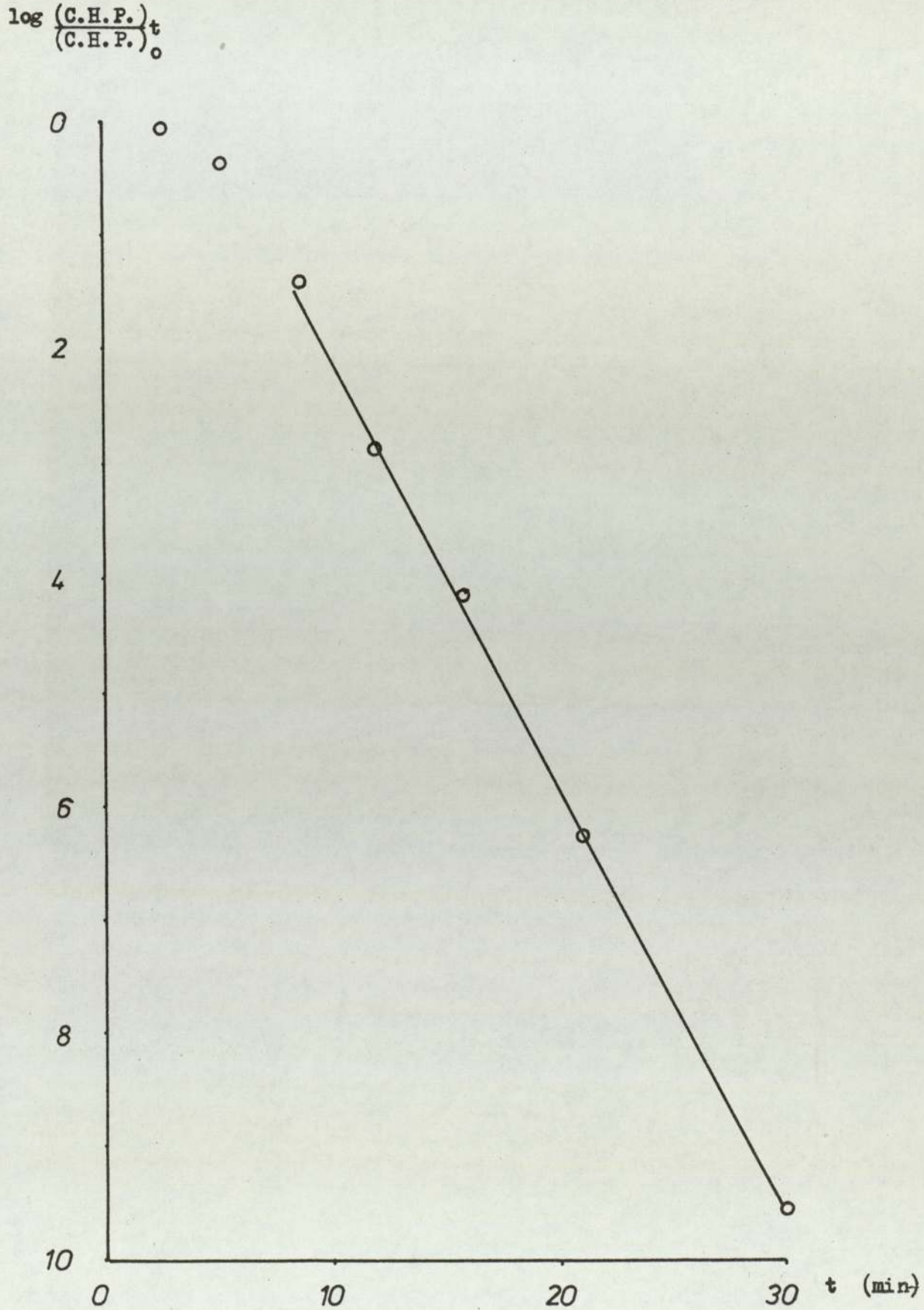
The shapes of the kinetic curves indicate a slow reaction followed by an apparent first order decomposition. Plots of concentration versus time were therefore constructed in order to measure the initial rates. The initial step was shown to be first order w.r.t. hydroperoxide, but over all the order is complex, until the formation of the catalytic species shows a pseudo first order hydroperoxide decomposition. The rate constant for the decomposition of E.B.H.P. (0.1 M.) in chlorobenzene using 2.6.4 (0.01 M.) at 75 C. was 2.62×10^{-3} sec^{-1}.

The reaction of E.B.H.P. with 2.6.4 was done in cumene; it was shown by G.L.C. that α-methyl styrene was a reaction product, and hence must originate from the solvent and not the hydroperoxide. The significance of these results are discussed in 5.2.

5.1.2 The reaction of the phenyl and isopropyl esters of catechol cyclic phosphate with cumene hydroperoxide. Results.

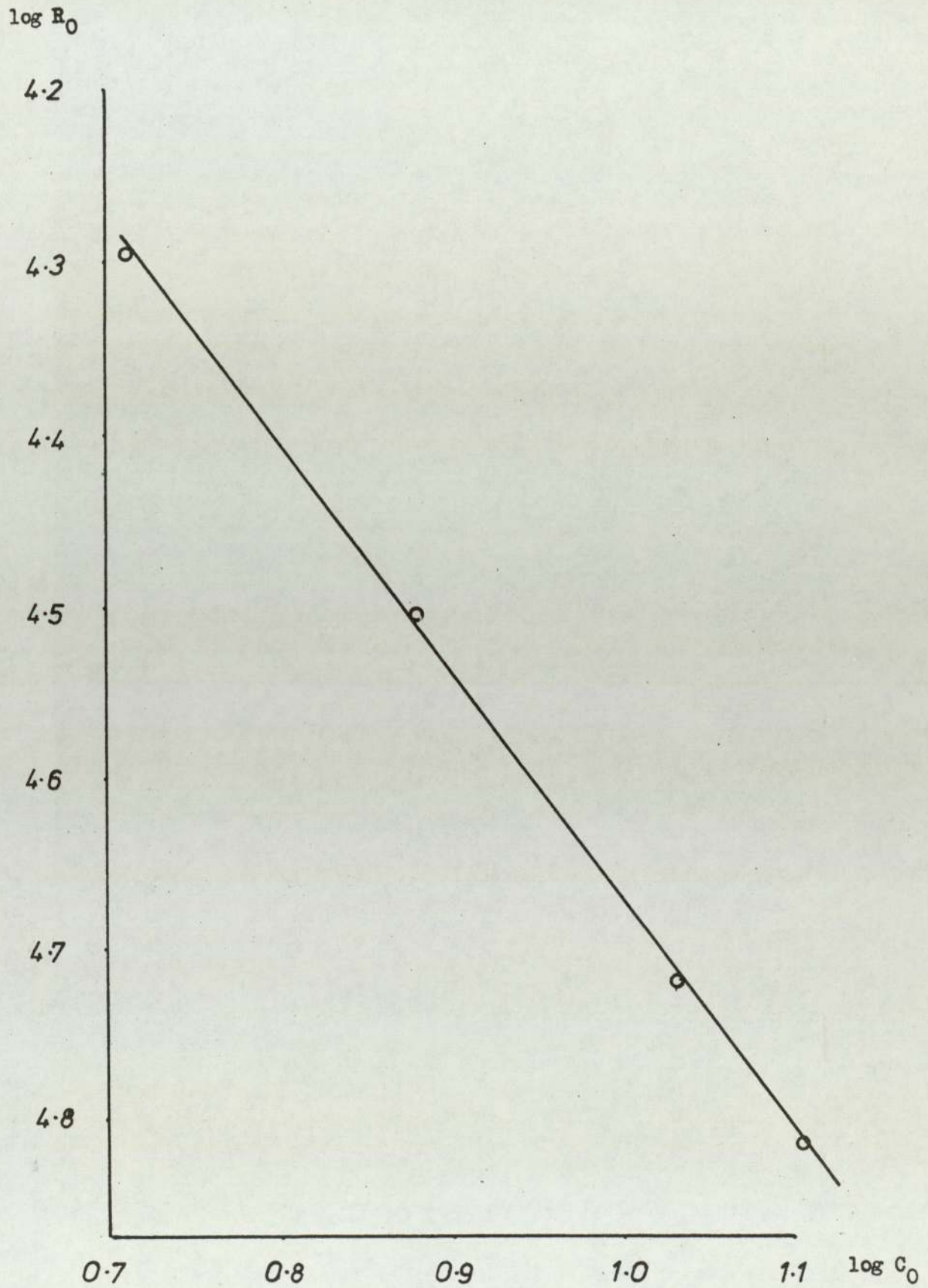
The reaction of 2-isopropxy-2-oxo-4,5-benzo-1,3,2-dioxa-phospholane (2.6.5.) with cumene hydroperoxide (CHP) was studied in a variety of solvents at different temperatures in order to study the effect of temperature, solvent, and dielectric constant on rate, and to look at any solvent oxidation products formed. Epoxidation and Baeyer Villiger reactions were attempted without

Fig XV



The decomposition of E.B.H.P. (0.1 mole) using 2.6.4. (0.01 mole) in chlorobenzene at 75°C

Fig XVI



Plot of initial rate versus initial concentration for the decomposition of E.B.H.P. using 2.6.4.

success, as the hydroperoxide decomposition products were those expected for the typical Lewis acid type of decomposition. Table XVI shows the first order rate constants for the reaction of CHP with 2.6.5 in a variety of solvents at different concentrations.

Table XVI

Rate constant sec^{-1}	Temperature °C	$\frac{(CHP)}{(2.6.5)}$	Solvent
8.74×10^{-4}	75	10	ØCl
6.90×10^{-4}	70	10	ØCl
4.07×10^{-4}	66	10	ØCl
2.27×10^{-4}	55	10	ØCl
9.48×10^{-5}	75	100	ØCl
4.53×10^{-4}	75	10	ØH
1.07×10^{-3}	75	10	$ØPr^i$

Table XVII shows the hydroperoxide decomposition products corresponding to the reactions in Table XVI.

Table XVII

Product distribution of the hydroperoxide decomposition with 2.6.5 in various solvents.

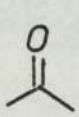
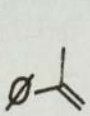
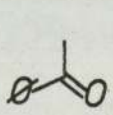
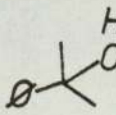
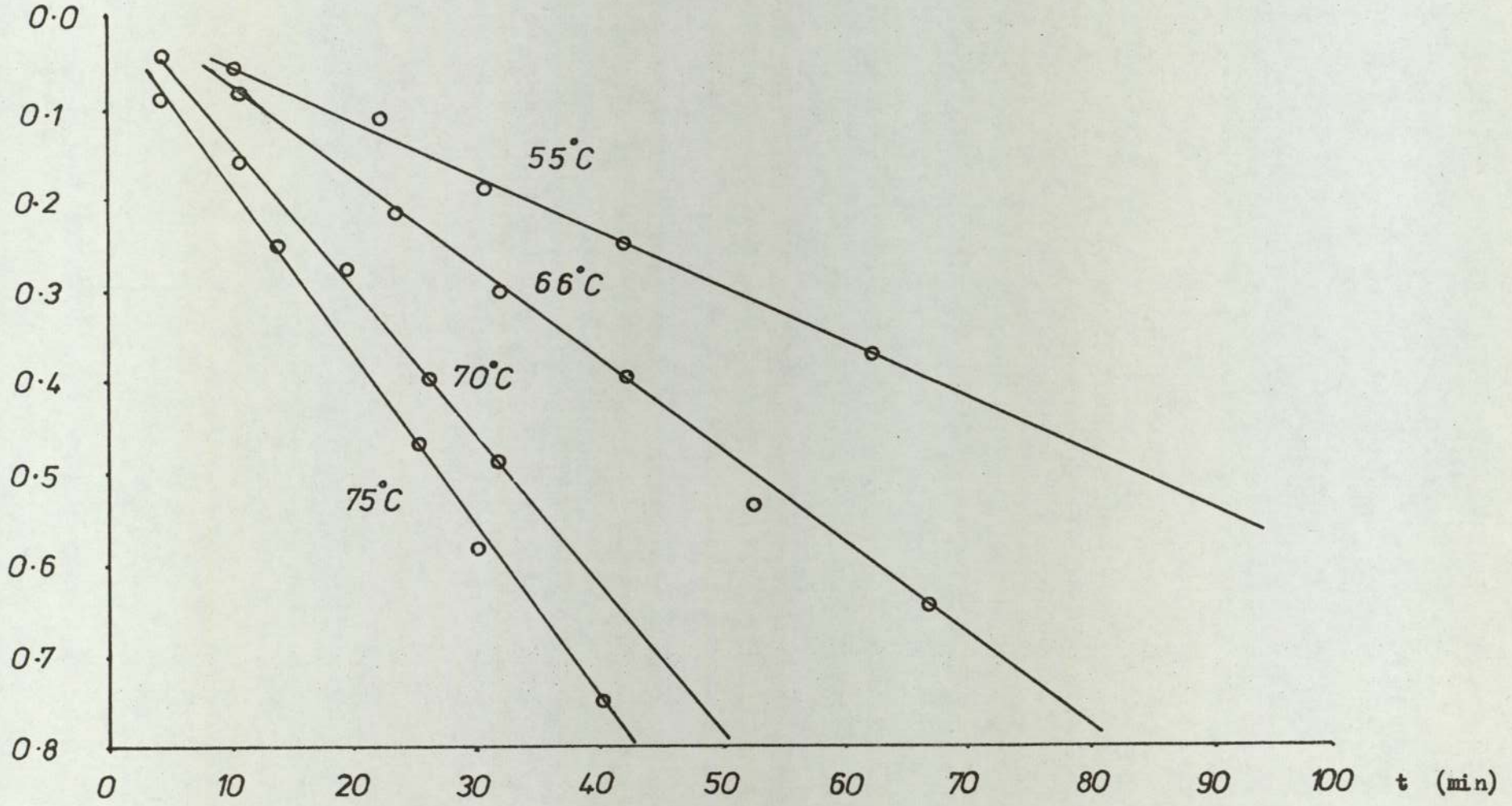
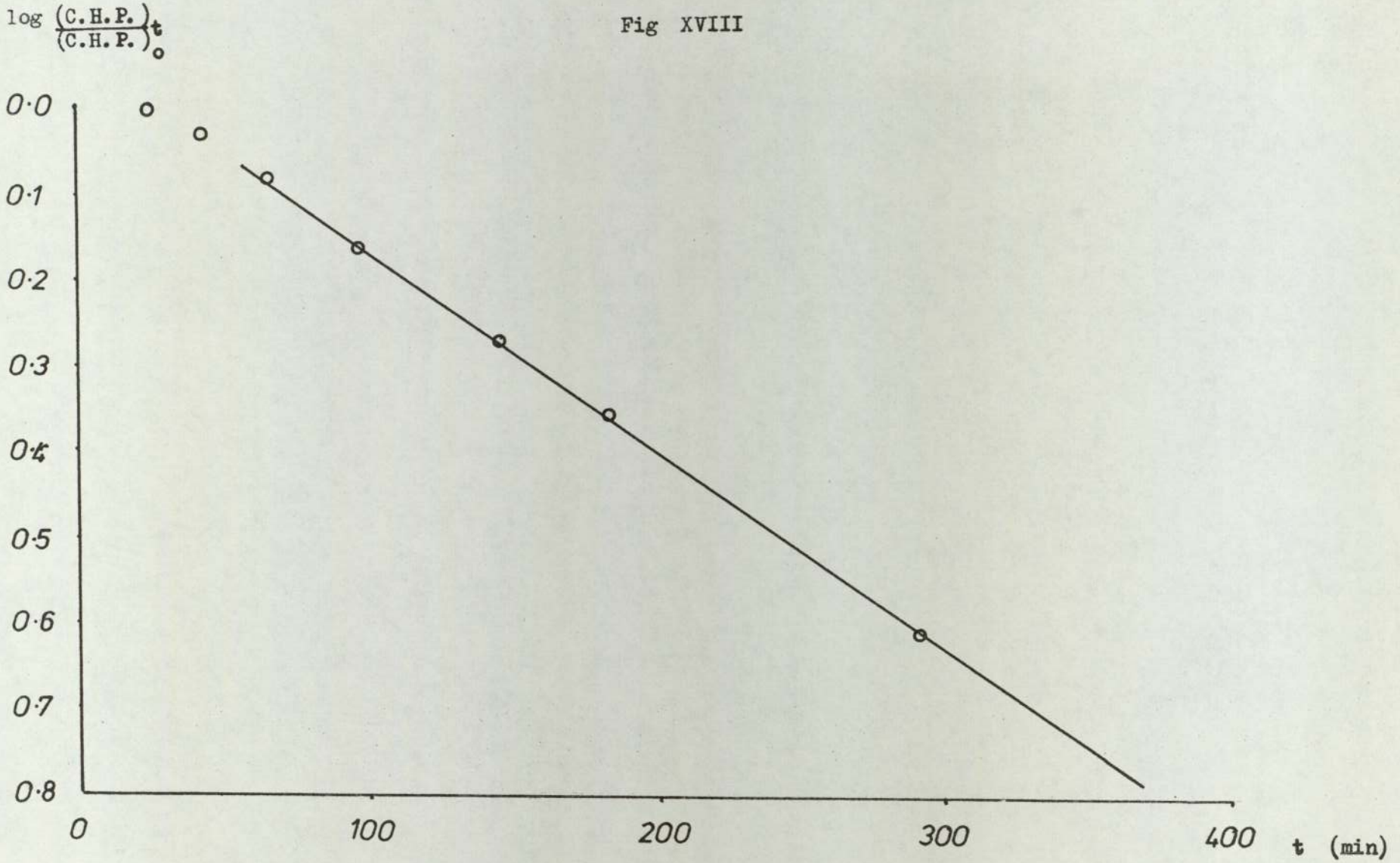
$\frac{(CHP)}{(2.6.5)}$	Temp. °C.	ØOH					Solvent
10	75	66.5	35.3	15.9	1.67	-	ØCl
10	65	66.25	42.95	10.5	1.38	4.08	ØCl
10	55	65.8	43.8	12.9	1.4	6.9	ØCl
100	75	70.9	40.0	14.8	1.0	4.7	ØCl
10	75	73.9	20.0	15.7	1.7	1.1	ØH
10	21	68.0	40.0	9.9	1.0	8.7	ØH
10	75	77.6	54.3	31.1	-	5.9	$ØPr^i$

Fig XVII



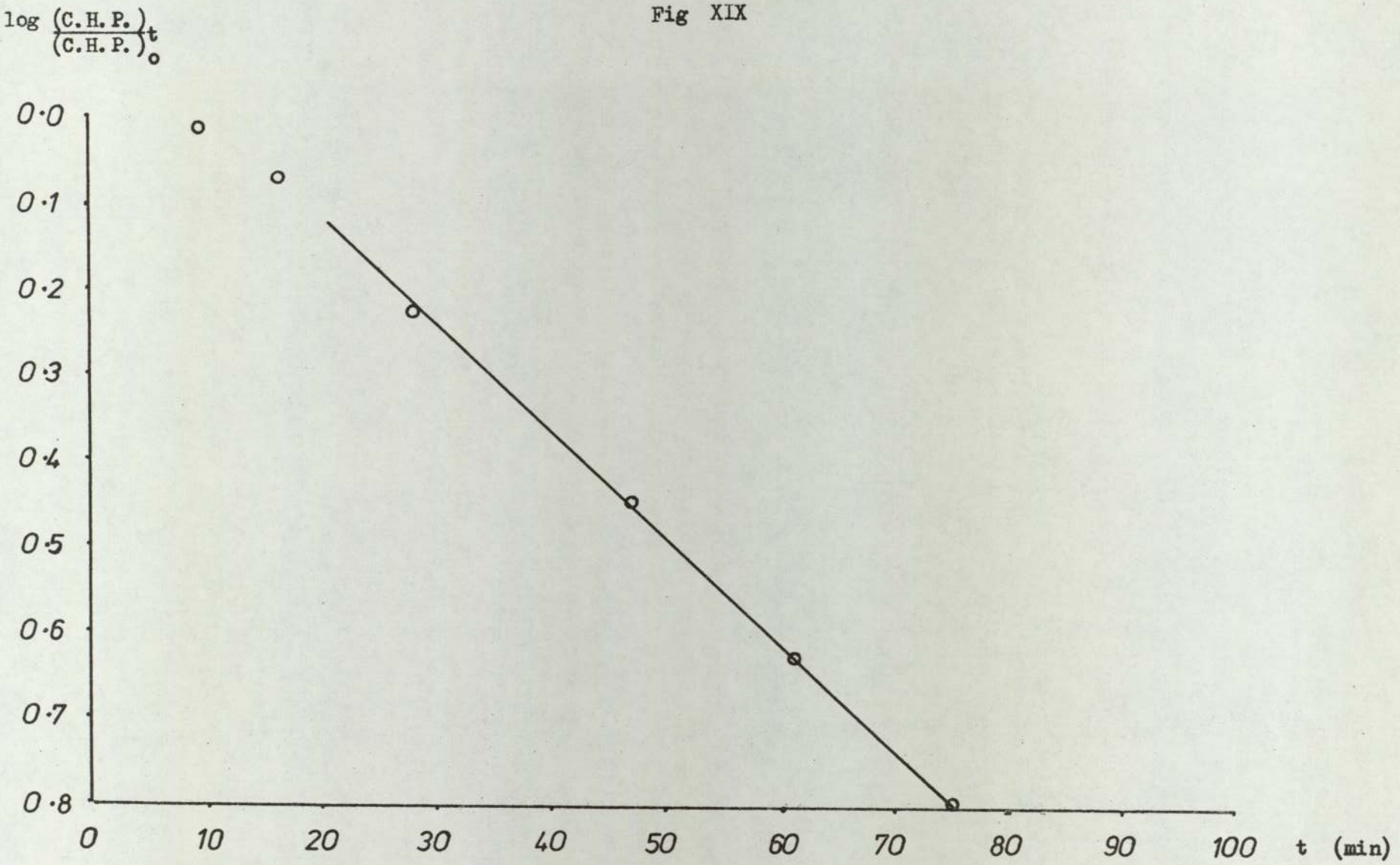
The decomposition of C.H.P. (0.1 mole) using 2.6.5. (0.01 mole) at various temperatures

Fig XVIII



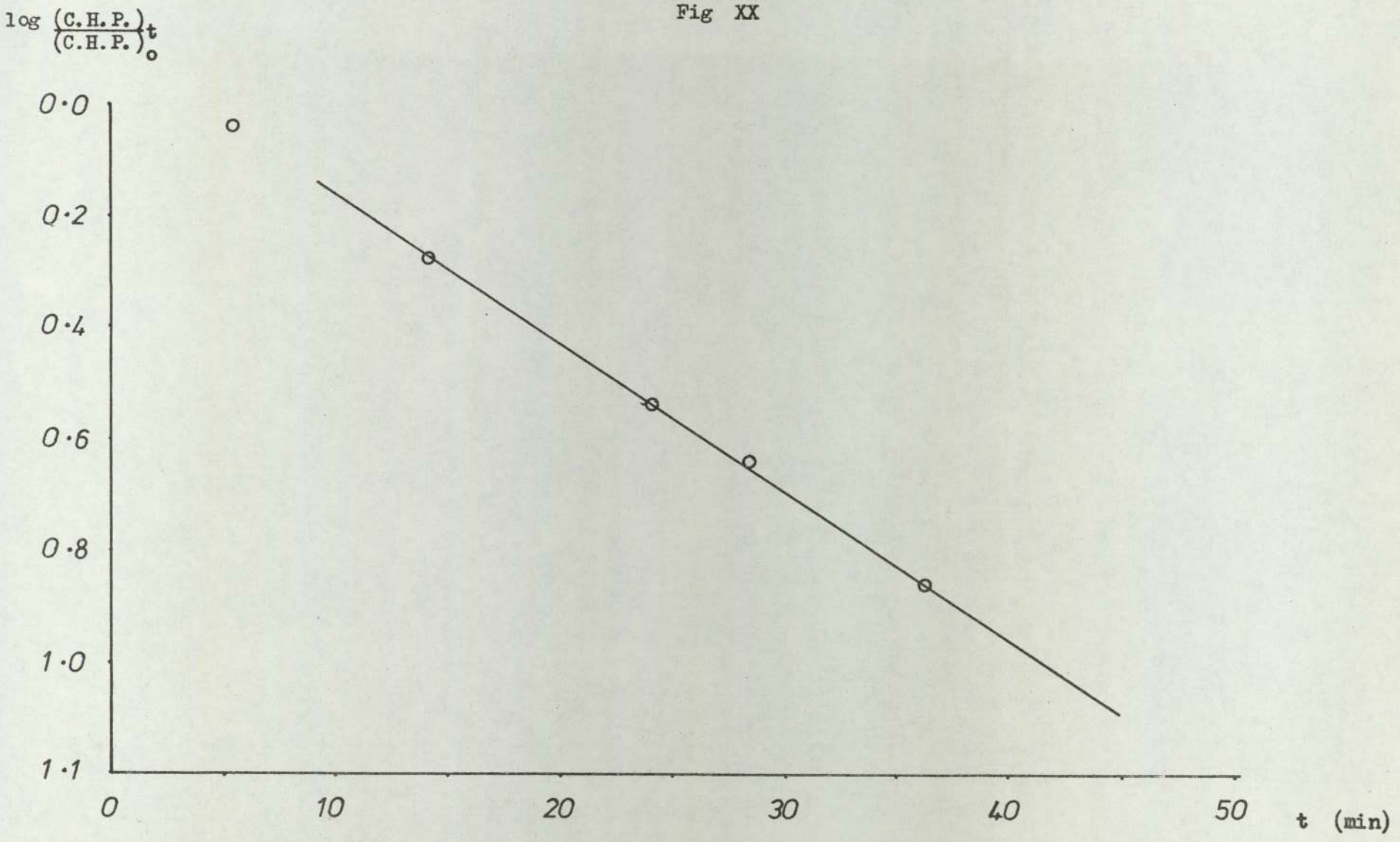
The decomposition of C H P. (0.1 mole) using 2.6.5. (0.01 mole) in chlorobenzene at 75°C

Fig XIX



The decomposition of C.H.P. (0.1 mole) using 2.6.5. (0.01 mole) in benzene at 75°C

Fig XX



The decomposition of C.H.P. (0.1 mole) using 2.6.5. (0.01 mole) in cumene at 75°C

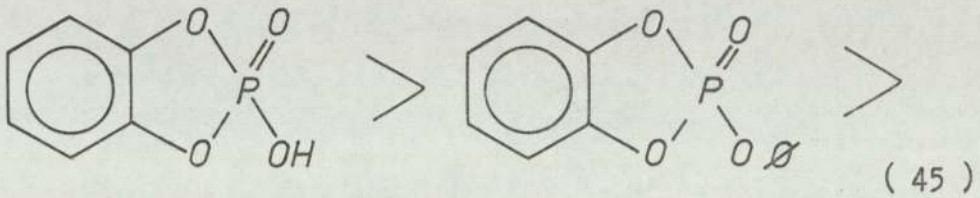
In order to study the effect of an aryl group on the rate of CHP decomposition, 2-phenoxy-2-oxo-4,5-benzo-1,3,2-dioxaphospholane (2.6.6) was prepared, and the kinetics of decomposition investigated in various solvents. The rate constants are summarized in Table XVIII.

Table XVIII

Rate constants for the reaction of (2.6.6) (0.01 M.) with CHP (0.1 M.) in various solvents.

Rate constant sec^{-1}	Solvent	$\frac{(CHP)}{(2.6.6)}$	Temp.° C.
5.71×10^{-3}	ØCl	10	75
8.51×10^{-5}	ØCl	100	75
1.12×10^{-2}	$ØPr^i$	10	75
5.50×10^{-3}	ØH	10	75

From these data it appears that the order of reactivity toward CHP is as follows (45).



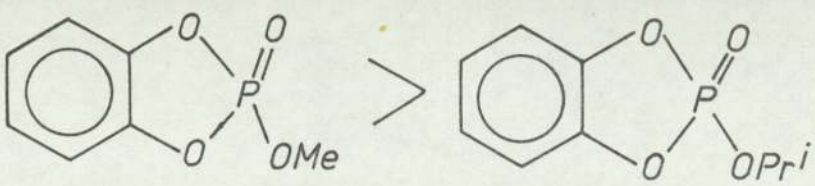
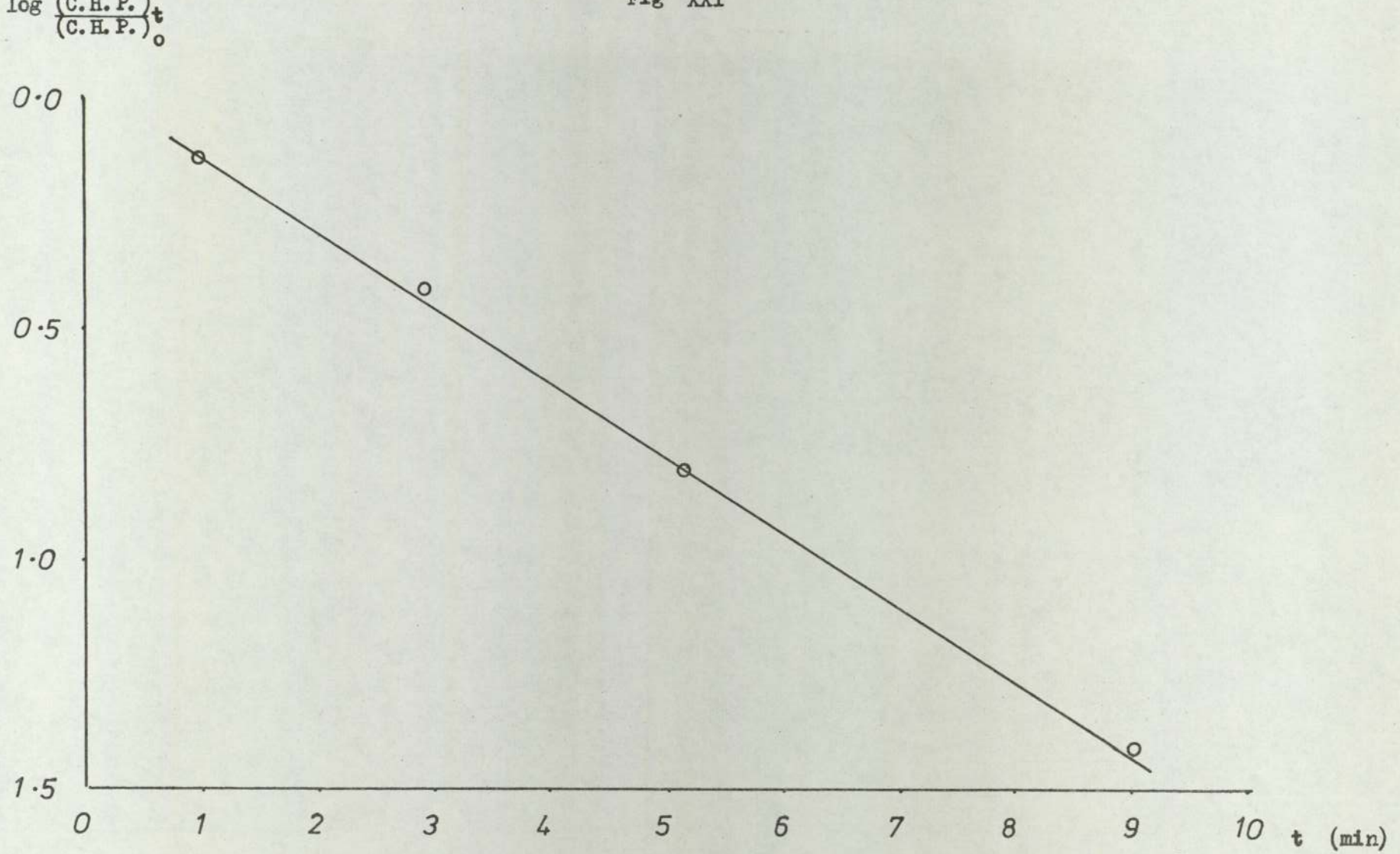
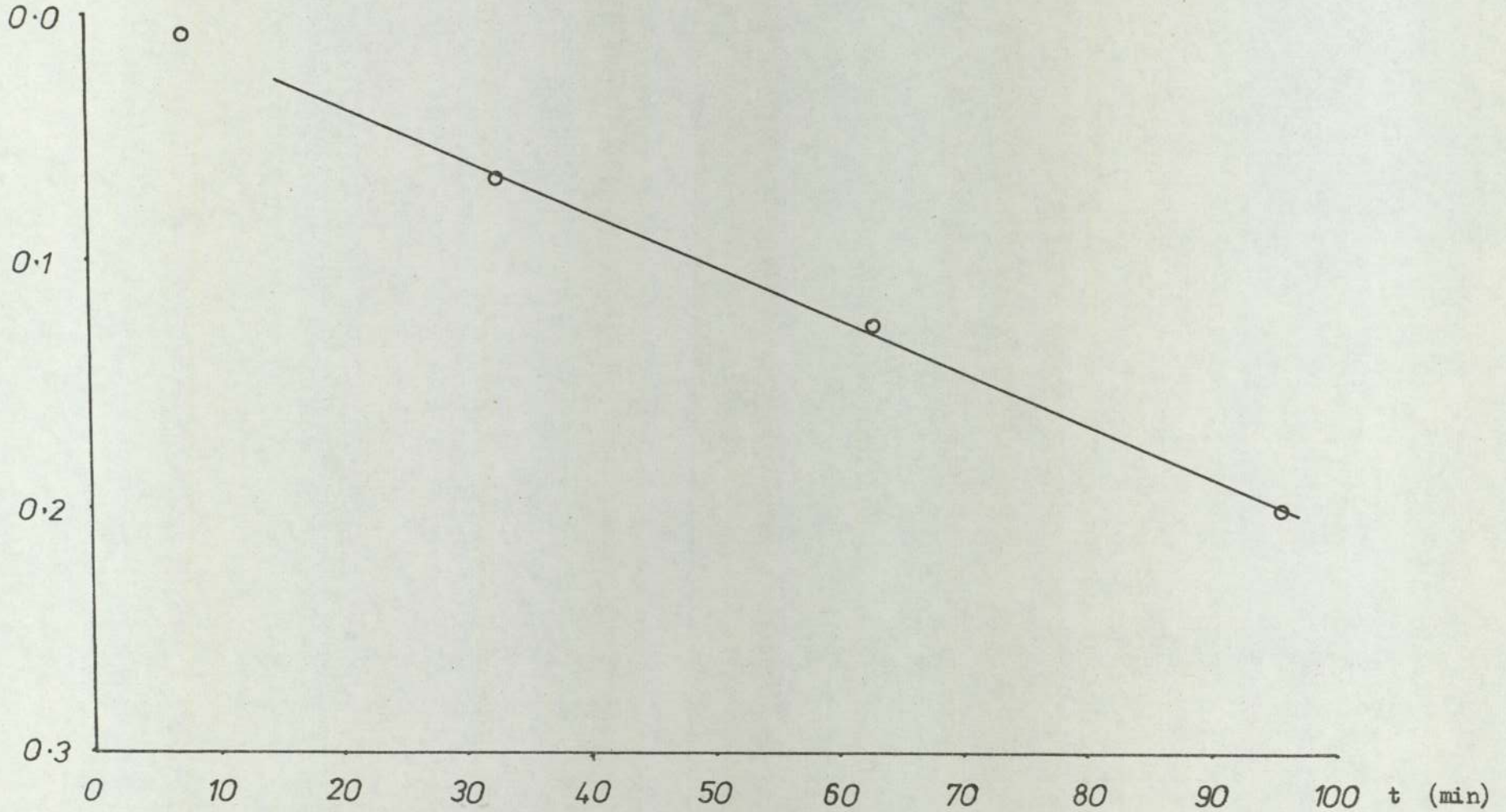


Fig XXI



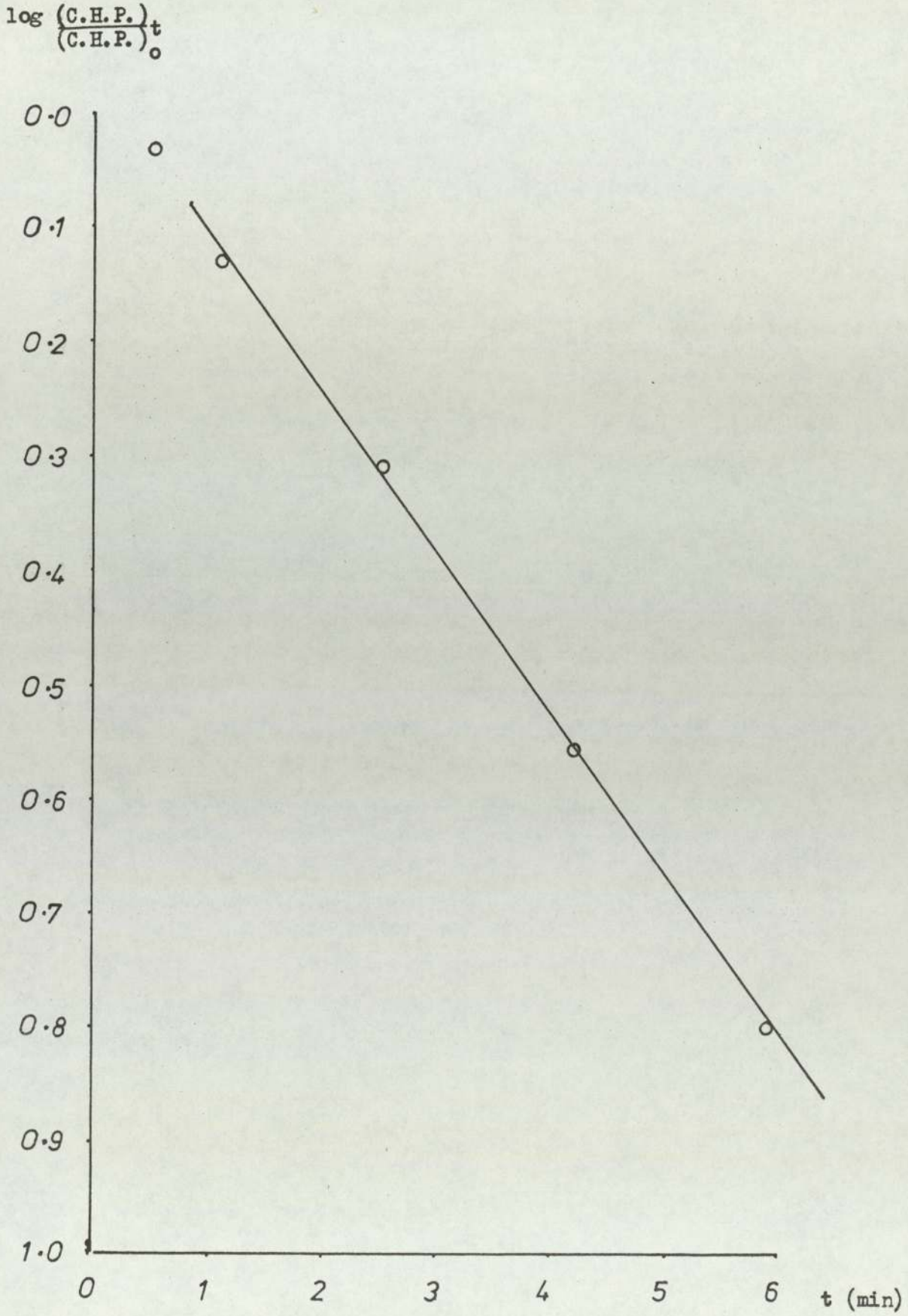
The decomposition of C.H.P. (0.1 mole) using 2.6.6. (0.01 mole) in chlorobenzene at 75 °C

Fig XXII



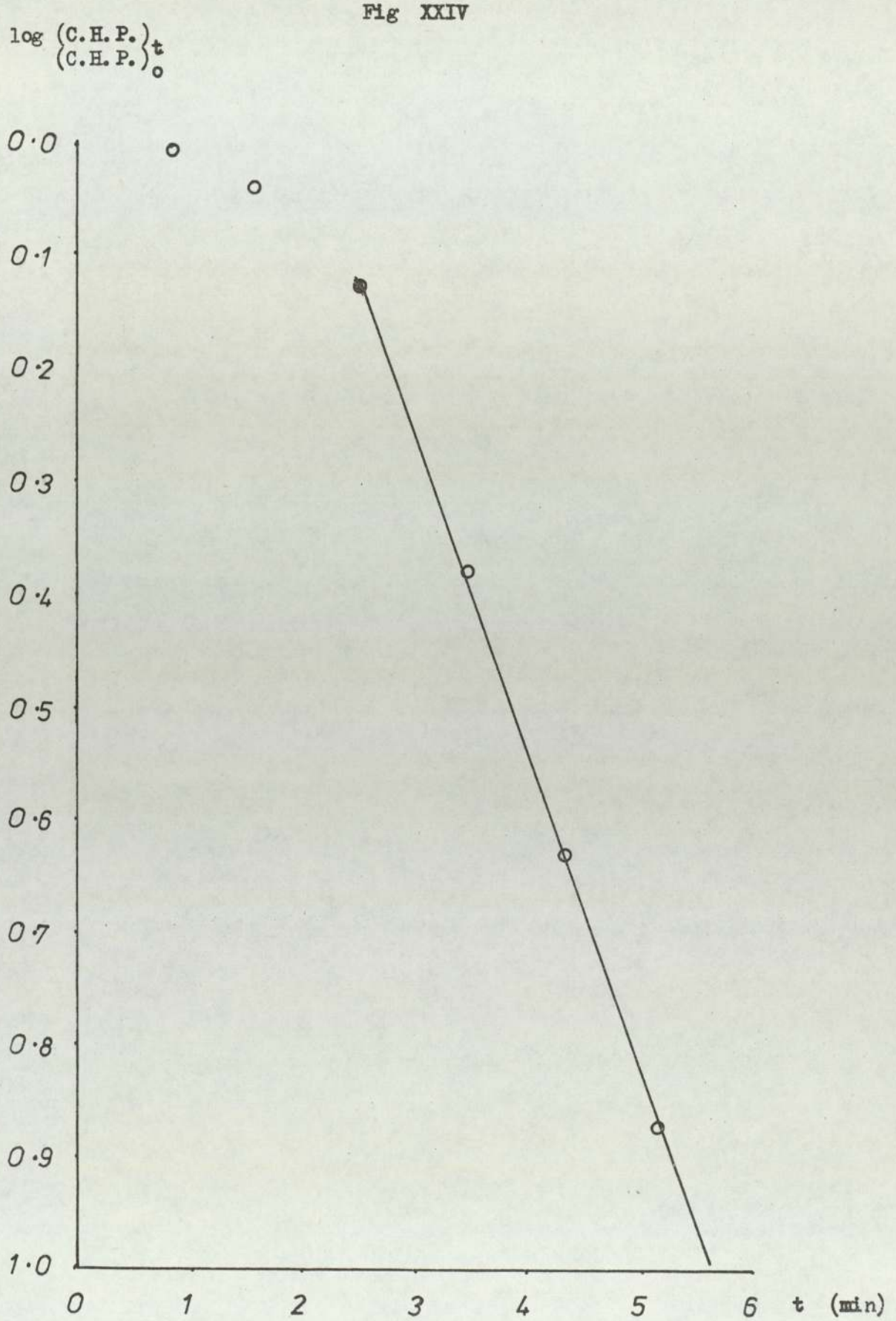
The decomposition of C.H.P. (0.1 mole) using 2.6.6. (0.01 mole) in chlorobenzene at 75°C

Fig XXIII



The decomposition of C.H.P. (0.1 mole) using 2.6.6.(0.01 mole) in benzene at 75°C

Fig XXIV



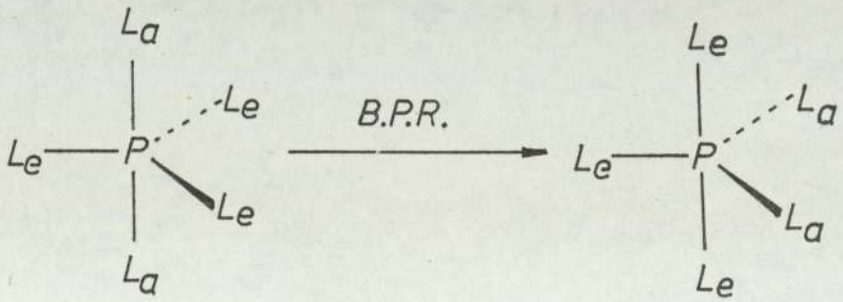
The decomposition of C.H.P. (0.1 mole) using 2.6.6. (0.01 mole) in cumene at 75°C

5.2 Results and discussion.

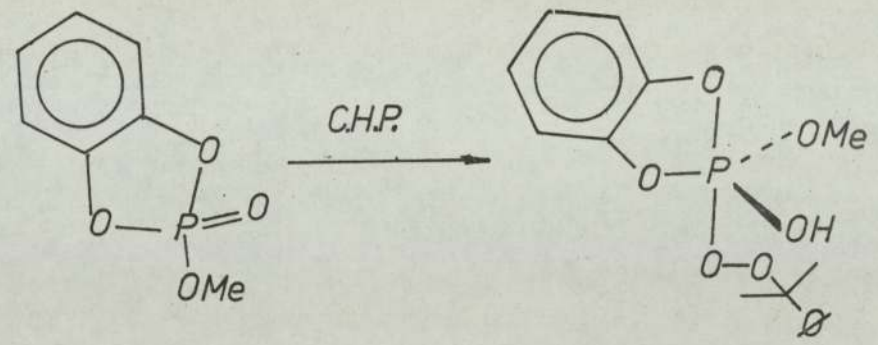
5.2.1 Phosphorus products.

N.m.r. measurements on the reaction of CHP with 2-methoxy-2-oxo-4,5-benzo-1,3,2-dioxaphospholane indicate that the methyl group in the catalyst, is not lost during the reaction, and so the catalytic species formed should contain the alkyl or aryl group. This was also shown by the difference in rate for the series in the last section (45). If the catalytic species had the same structure, in all cases, all the rates should be equal.

The catalytic effect of the catechol phosphates and the retention of the alkyl group during reaction can be explained in terms of pseudorotation about the phosphorus atom. The concept of pseudorotation was first introduced by Berry (79) to explain the rapid intramolecular exchange of fluorine atoms between apical and equatorial sites in phosphorus pentafluoride. A single Berry pseudorotation interchanges the apical ligands La with two of the three equatorial ligands Le, the third "pivot" ligand remains in the original site.

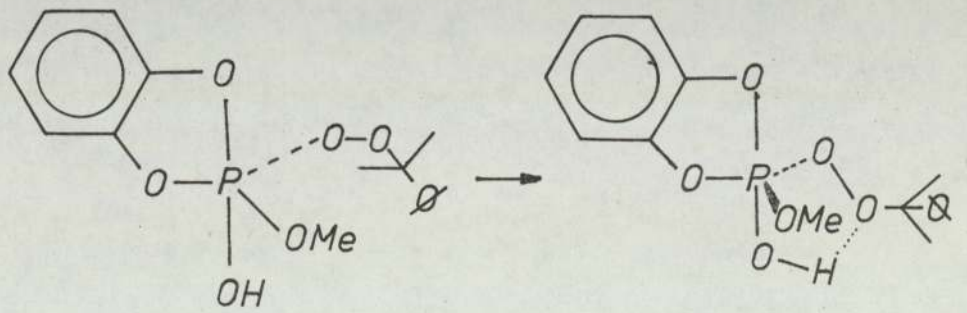


However the following considerations must be taken into account [80] ; (a) the most electronegative ligands preferentially occupy apical sites, (b) if a small ring is present, the ring prefers to span an axial and an equatorial position, (c) ring strain decreases on reaction of nucleophiles with phosphoryl phosphorus [75] . These observations will be discussed fully in the hydrolysis section. If cumene hydroperoxide attacks 2.6.4 at phosphorus, the following pentacoordinate species is possible. (46).



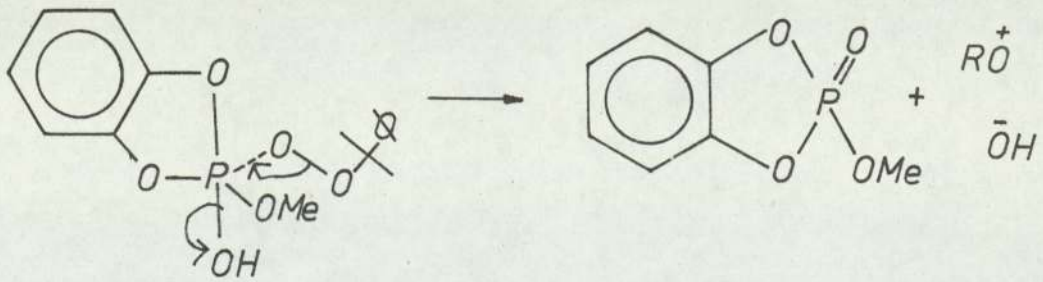
(46)

The resulting pentacoordinate species can then undergo pseudo-rotation to place the hydroxyl group in an axial position (47).

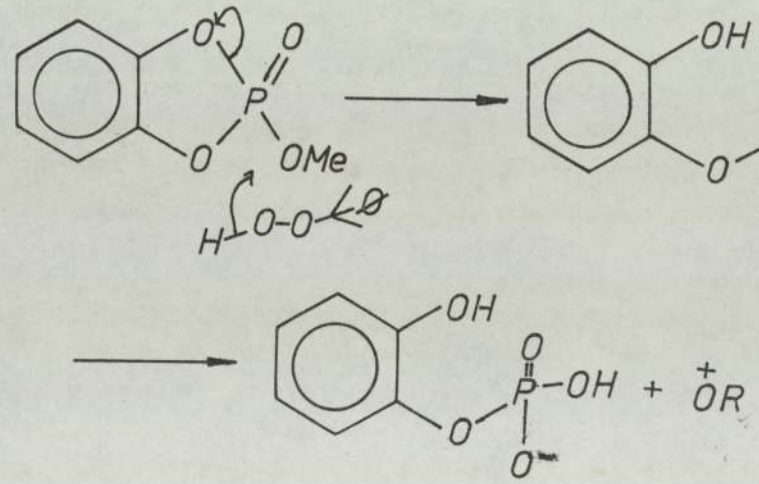


(47)

Decomposition can then take place, as the axial hydroxyl group is in the most favourable leaving position,

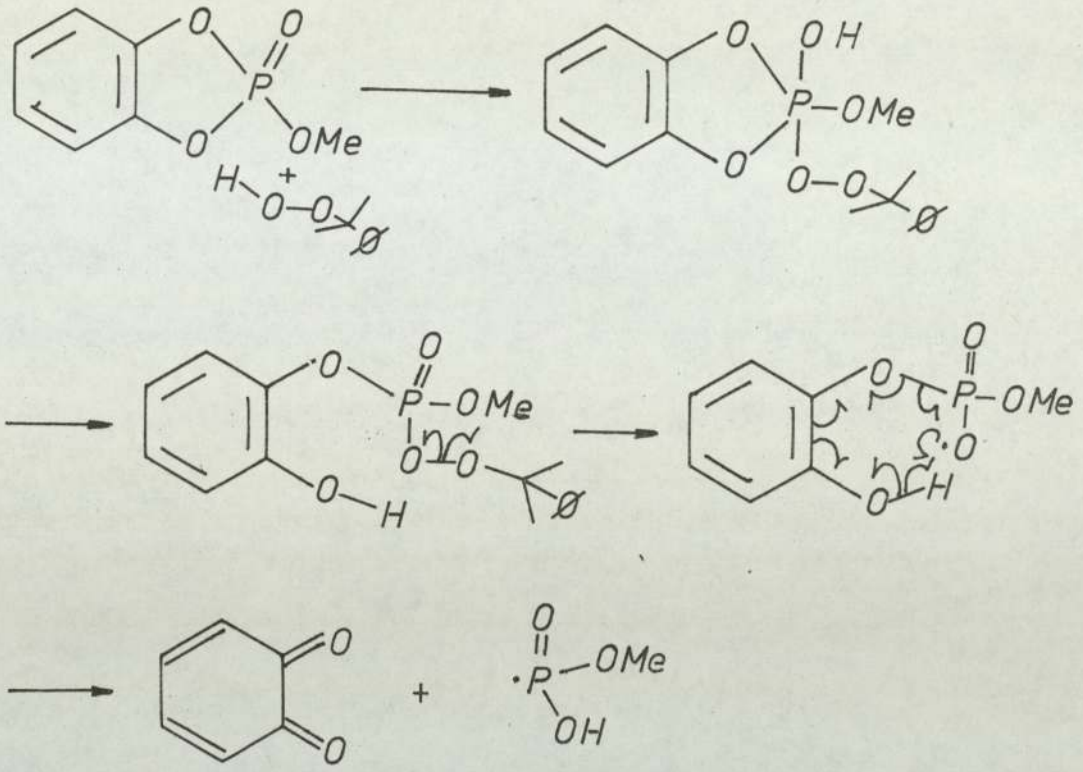


and hence the catalyst is regenerated, with methyl group intact. After the reaction has gone to completion however, many other phosphorus products were isolated from the reaction mixture; these included catechol cyclic phosphate, o-hydroxy-phenylphosphate, and o-benzoquinone. Catechol cyclic phosphate almost certainly results from the attack of hydroxyl ion on 2-methyloxy-2-oxo-4,5-benzo-1,3,2-dioxaphospholane followed by pseudorotation, (see hydrolysis section). o-Hydroxyphenylphosphate can result from several paths; one of which involves the SN_2 type of displacement with hydroperoxide, not including pseudorotation (48).

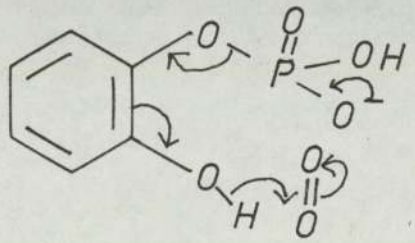


(48)

o-Benzoquinone probably results from a free radical reaction, and was only observed when large quantities of catalyst were present, (> 1:1 stoichiometry). In the presence of radical traps, the quantity of o-benzoquinone was greatly reduced; a possible mechanism for the production of o-benzoquinone is as follows (49).



It was shown that singlet oxygen (81) did not oxidize o-hydroxyphenyl-phosphate to o-benzoquinone, and so small amounts of the latter, if it was produced in the hydroperoxide reaction mixtures, would not be responsible for the o-benzoquinone produced e.g.



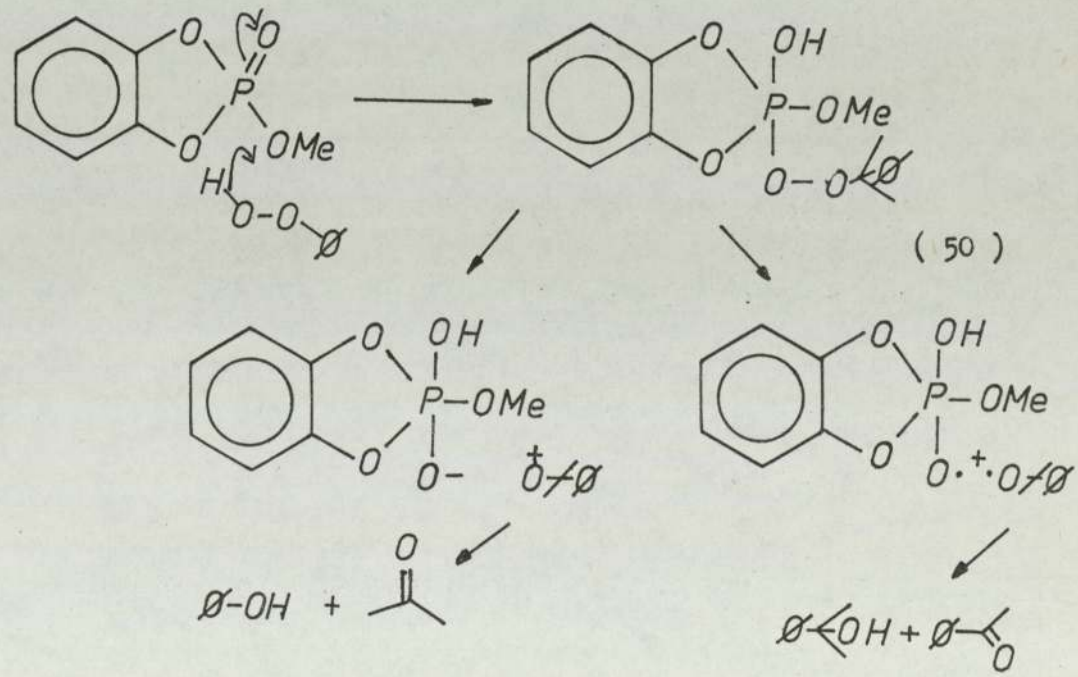
does not occur

5.2.2 Hydroperoxide decomposition products:- mechanistic implications.

The products of hydroperoxide decomposition were given in section 5.1; these are of importance as they can give information

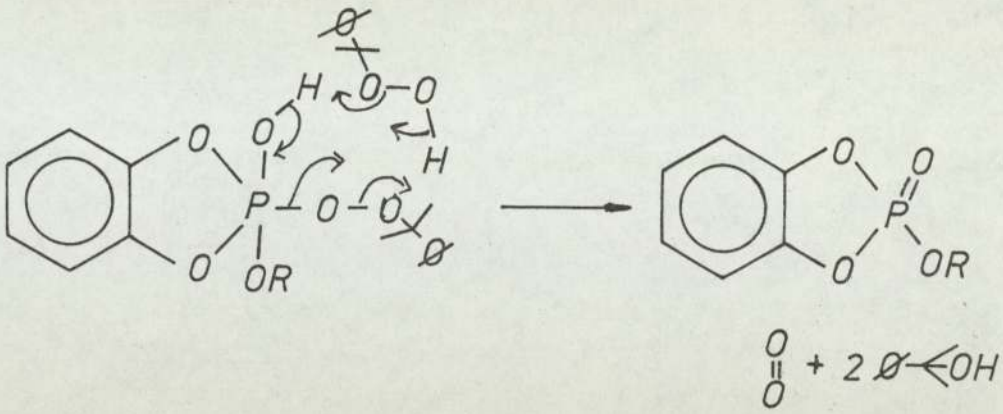
about the mechanism of a reaction[71]. The rate enhancement noted in nitrobenzene is consistent with an ionic mechanism[82], and the main products of CHP decomposition with all the catechol cyclic esters were phenol and acetone. With E.B.H.P. the main products were phenol and acetaldehyde, in agreement with the mechanism postulated by Humphris and Scott[16] for the decomposition of CHP with catechol cyclic phosphate.

It was shown however, that at higher concentrations of 2-alkoxy-2-oxo-4,5-benzo-1,3,2-dioxaphospholane, considerable quantities of α-methyl styrene were formed. This could be due to a dual mechanism involving free radicals (50).



The cumyl alcohol formed can undergo dehydration to give α-methyl styrene[76]. However, only very small amounts of acetophenone occur in the product analysis, and an ionic mechanism was postulated

involving an extra molecule of hydroperoxide[77] (51),

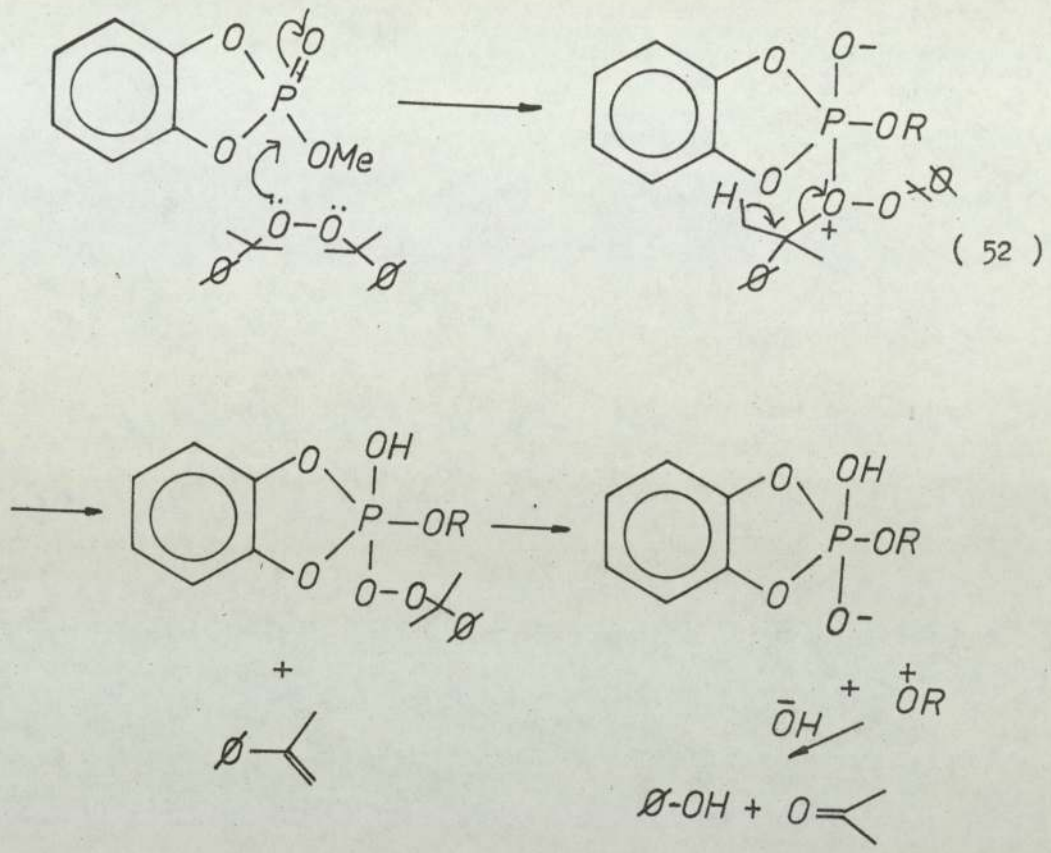


(51)

however, no oxidation products were observed using chlorobenzene as solvent, and no gas evolution was detected. The mechanism may be more important in other solvents.

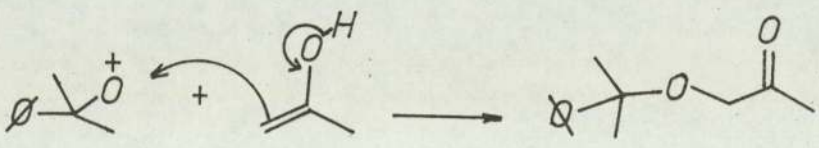
It was shown, that compounds 2.6.4 to 2.6.6* readily decomposed dicumyl peroxide. The products of decomposition were solely α-methyl styrene, phenol and acetone. The kinetics of decomposition were followed by the appearance of phenol using G.L.C., the first order rate constant was found to be 1.46×10^{-4} $sec.^{-1}$, following a pseudo first order hydroperoxide decomposition. (Fig.XXV). As dicumyl peroxide is readily formed from cumene hydroperoxide in the presence of Lewis acids[83], or charcoal[73], it seems likely that part of the α-methyl styrene formed, originated from dicumyl peroxide by the following mechanism (52).

*see appendix



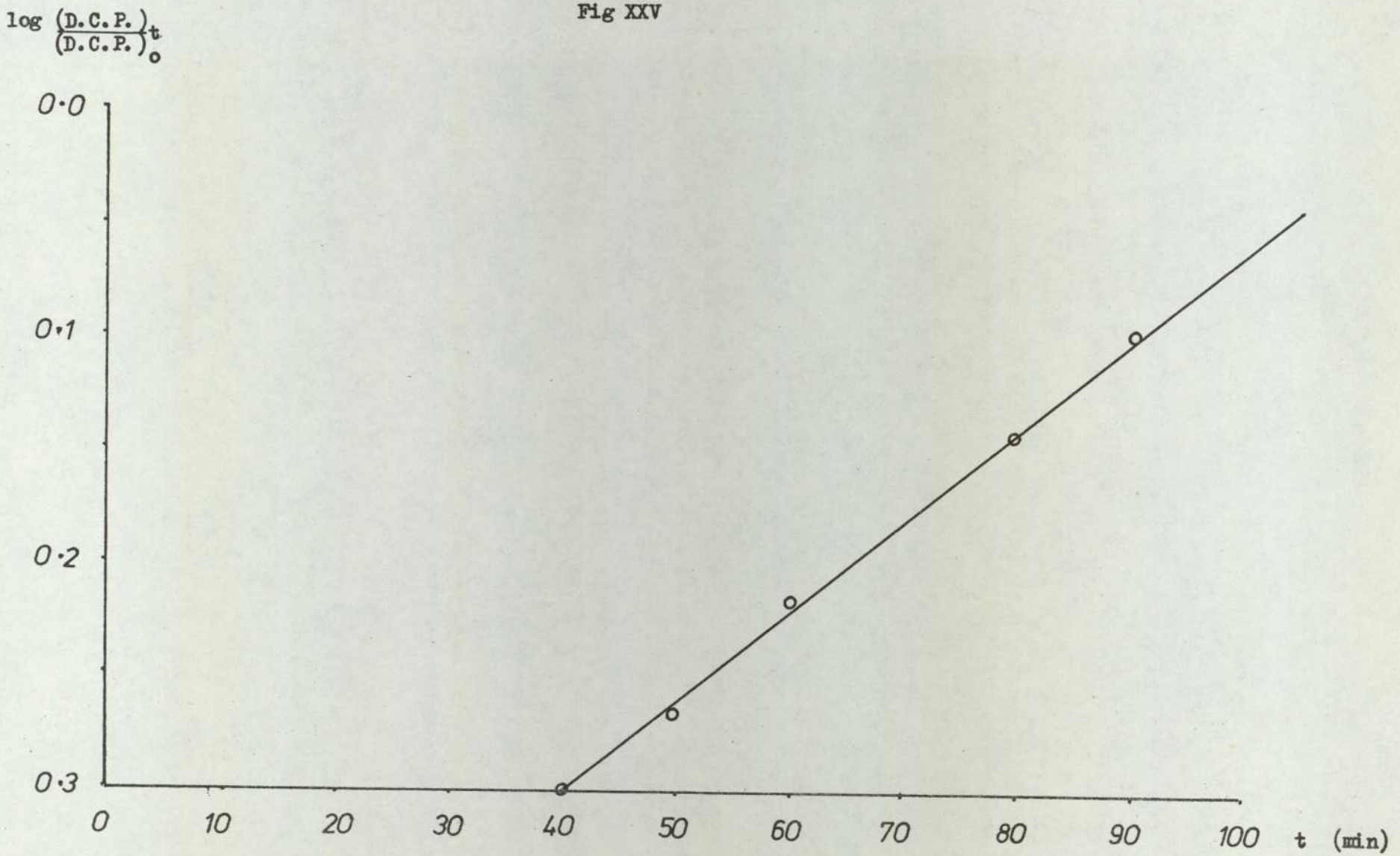
(52)

It was found that less than the expected amount of acetone was produced in all the decompositions involving cumene hydroperoxide; as care was taken to cool the sample before G.L.C. analysis, evaporation of the acetone is not a satisfactory explanation. Seubold et al.[84] reported similar results. One possibility is that acetone itself reacts with the oxonium ion produced from the hydroperoxide (53).



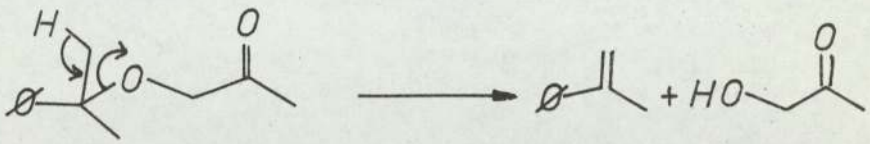
(53)

Fig XXV



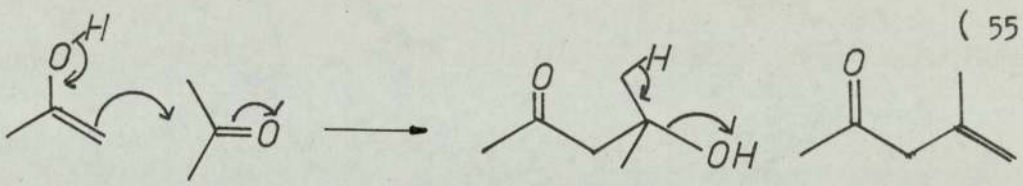
The decomposition of dicumyl peroxide (0.1mole) using 2.6.4. (0.01 mole) in chlorobenzene at 75°C

The resulting ether could give α-methyl styrene and hydroxy-acetone (54).



(54)

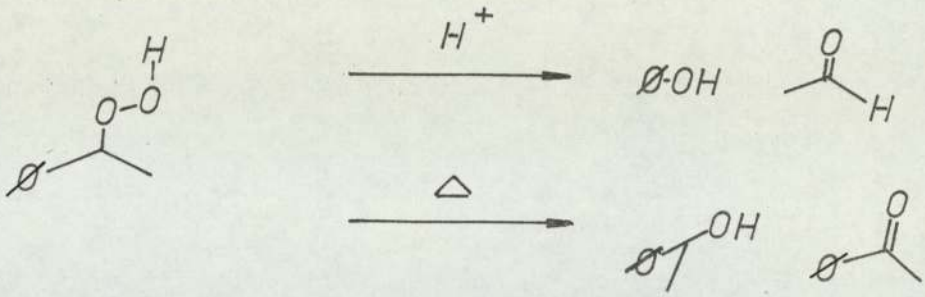
Mesityl oxide was detected in the reaction mixture, and this must result from self condensation of the acetone, in the presence of the cyclic phosphate (55),



(55)

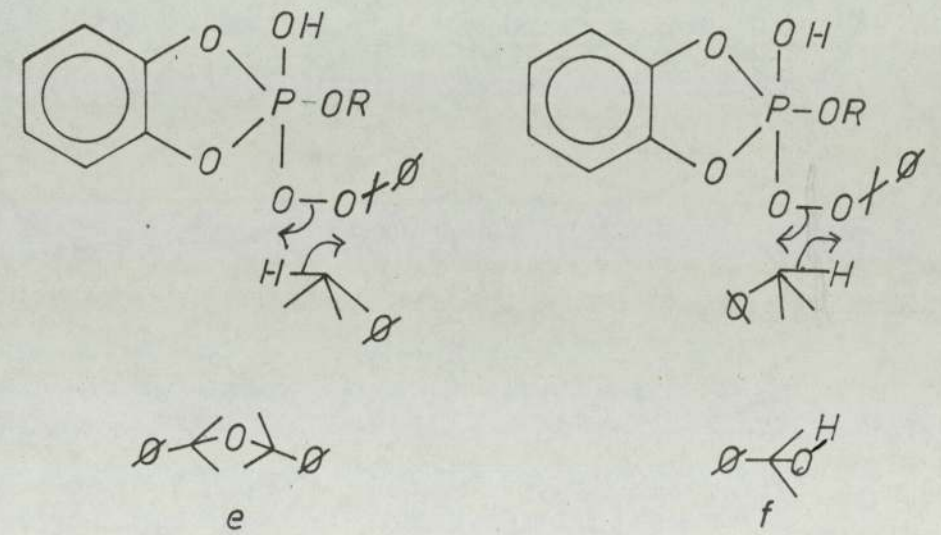
thus the non equivalence of phenol and acetone was explained. Decomposition reactions were carried out using acetone as a solvent to verify reaction (53); however, acetone was found to react with the cyclic phosphates, and the reaction proceeded very slowly, some α-methyl styrene was formed, but the results were not conclusive.

C.H.P. decomposition reactions carried out using cumene as a solvent, produced larger amounts of α-methyl styrene than expected. Using E.B.H.P., α-methyl styrene was still produced. As E.B.H.P. itself cannot give α-methyl styrene from either free radical or ionic decomposition (56),



(56)

the α-methyl styrene must come from the solvent. As traces of dicumyl ether were formed in the reaction mixture (identified by G.L.C./ mass spec.) the formation of α-methyl styrene from the interaction of active oxygen with cumene was ruled out. It seems possible however, for cumene to react with the phosphorus peroxy intermediate (57)



(57)

e

f

(f) is more likely on steric grounds, and would give rise to the excess α-methyl styrene observed, as the catechol phosphates have been shown to be effective dehydrating agents for cumyl alcohol (76).

In order to study the initial slow reaction observed in all the phosphate-hydroperoxide decompositions (Fig. XV), the tangent at t = 0 for plots of concentration versus time for

different hydroperoxide concentrations was determined, thus if

$$R_{initial} = -\left(\frac{dc}{dt}\right)_{initial} = KCo^{n} \times \prod (\text{ other concentrations })$$

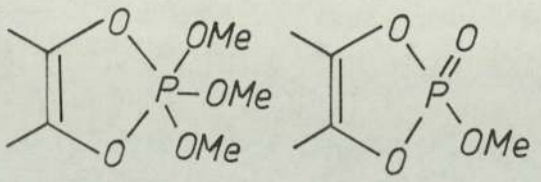
$$\log R_{initial} = \log K + n \log Co + \log (\text{ other concentrations })$$

Thus a plot of log R initial vs. log Co was constructed, and the slope was found to be 0.9545 e.g. $\simeq$ unity. Thus it was shown that initially the reaction is first order with respect to hydroperoxide; over all however, the order was complex, and no simple expression could be produced. After the initial step (which may involve a change in mechanism and hence explain the complex order), a pseudo first order reaction followed, and it was shown that many hundreds of moles of hydroperoxide could be destroyed by the catalytic species generated. For 2-methoxy-2-oxo-4,5-benzo-1,3,2-dioxaphospholane, the value of Ea for the reaction with cumene hydroperoxide, was shown to be 11.7 K calc. mole^{-1}. This result is similar to those obtained for the reaction between methyl iodide and substituted dimethylanilines[85], and is consistent with an ionic mechanism passing through an ordered transition state.

5.2.3 The reaction of hydroperoxide with other phosphate systems containing catalytic activity.

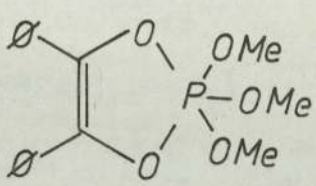
From the previous discussion it can be seen that a vast difference exists between the reaction of aliphatic and aromatic

cyclic phosphates with hydroperoxide. It was therefore thought pertinent to synthesize other cyclic phosphates with similar features to the aliphatic and aromatic series, and also to investigate the effect of ring size on the hydroperoxide reaction. The following compounds were synthesized and an explanation is given as to why each were chosen.

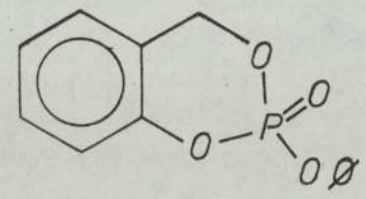


I

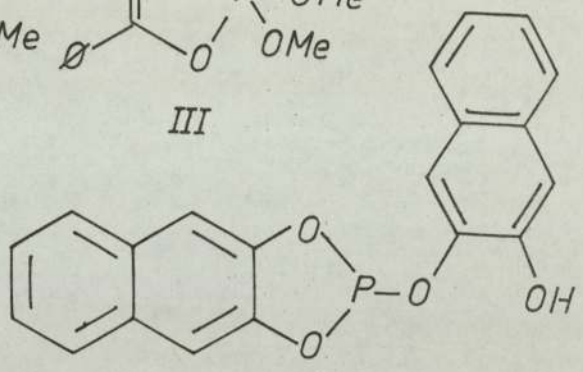
II



III



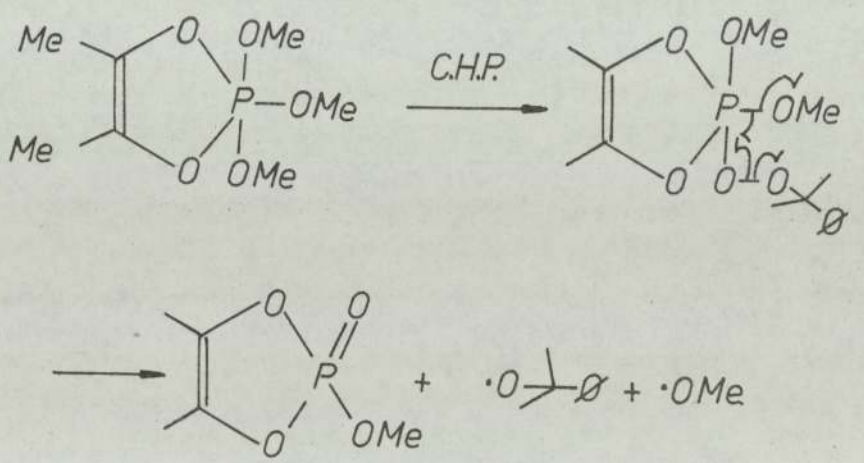
IV



V

Compounds I and II were tried; II contains a strained ring, and a double bond, so that the idea of an Sp^2 hybridized carbon affecting the catalytic hydroperoxide decomposition could be investigated, however, these compounds contain methyl groups and hence the + I effect could reduce the effectiveness of II as a catalyst for hydroperoxide decomposition, as the Lewis acidity of phosphorus is lowered. Compound III was used because the effect of increased conjugation could be studied. Compound IV was synthesized in order to study the effect of ring strain, and V increased

conjugation by a naphthyl group directly fused to the ring. It was found that compounds I, II and III were catalysts for hydroperoxide decomposition, but a maximum of five moles of hydroperoxide was consumed. The reaction gradually slowed down after four moles of hydroperoxide had been destroyed. The rate constant for the reaction of I with a ten mole excess of C.H.P. was determined as 2.41×10^{-5} sec.$^{-1}$ after an initial fast reaction, possibly involving displacement of methoxy ion by hydroperoxide (58) (see appendix for decay curve).



(58)

Compound IV was found to be inert to hydroperoxide; no reaction occurred with C.H.P. over a period of 24 hr. in catalytic amounts. This shows that the five membered ring is important in the catalytic decomposition of C.H.P. Hydrolysis studies[86] on six membered rings have shown that a pentacoordinate sp^3d square pyramidal intermediate is formed with OH at the apex[86], and not a pentagonal bipyramid as in the five membered ring intermediate.

The six membered ring has the normal Td bond angles, and these structural features contribute to the stability of the molecules compared with the five membered cyclic phosphates. The activation energy for the hydrolysis of six membered cyclic phosphates is normally high compared with the five membered rings, which exhibit low activation energies[86]. From these data, it can be seen that six membered cyclic phosphates possess little or no ring strain, and as an entirely different mechanism of hydrolysis was observed, (e.g. the five membered rings are hydrolysed by a unique mechanism involving pseudorotation), it appears that ring strain and hence the presence of a five membered ring are important features of the peroxide decomposing activity observed. The six membered ring lacks strain and behaves as a normal alkyl phosphate, toward hydroperoxide e.g. triphenylphosphate is inert toward hydroperoxide[76].

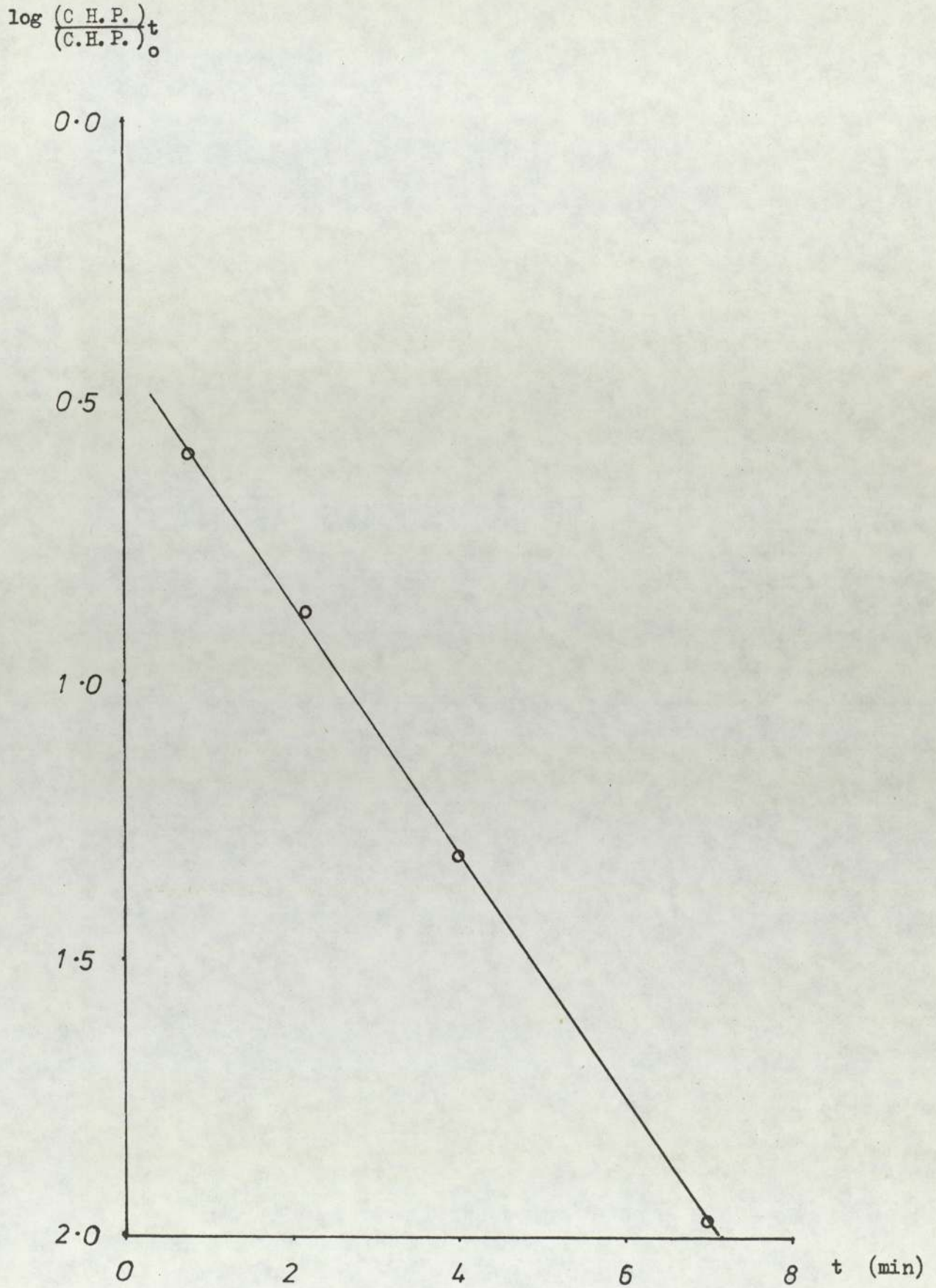
The reaction of C.H.P. with compound V was studied. Initially second order kinetics was observed, and both first order w.r.t C.H.P. and phosphite;

$$\frac{d(CHP)}{dt} = K_2(CHP)(\text{phosphite})$$

followed by a pseudo first order reaction. The first stage involved the oxidation of the phosphite to phosphate[87][76], (59).

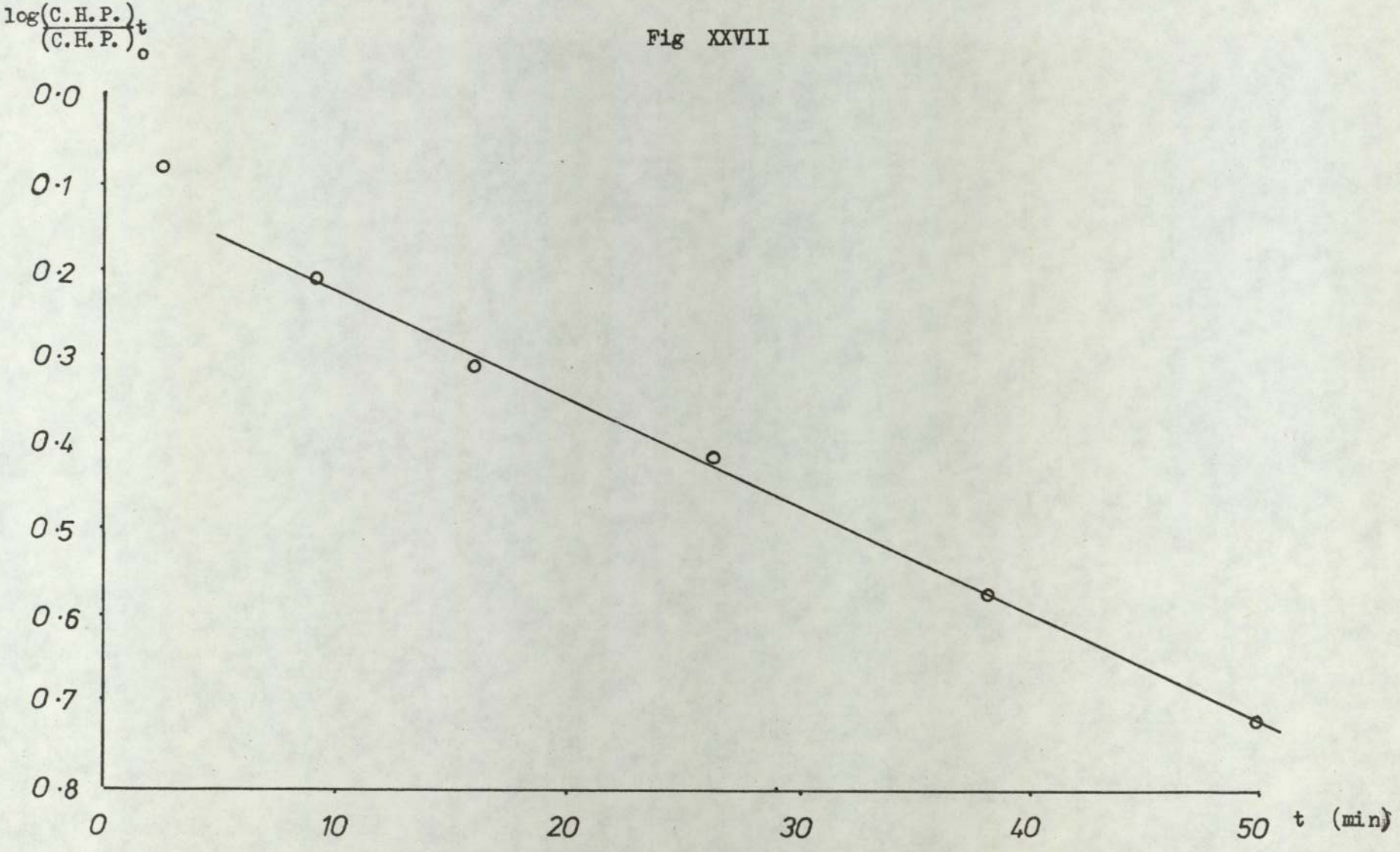
$$RO_2H + (RO)_3P \longrightarrow (RO)_3P{=}O + ROH \qquad (59)$$

Fig XXVI



The decomposition of C.H.P. (0.1 mole) using 2.6.12. (0.01 mole) in chlorobenzene at 75°C

Fig XXVII



The decomposition of C.H.P. (0.1 mole) using 2.6.12. (0.001 mole) in chlorobenzene at 75°C

The second stage was the slow reaction described in 5.2.2. (p118); the third step involved a very strongly catalytic pseudo first order decomposition. The rate for a 10 : 1 mole ratio of hydroperoxide : catalyst was much faster than that observed for any of the catechol series; the intermediate peroxy species is therefore less stable than the catechol derivative. This must be due to the increased conjugation in the naphthyl ring, allowing a highly ionic transition state. The products from the catalytic decomposition were solely phenol and acetone, only the α-methyl styrene resulting from dehydration of cumyl alcohol from the phosphite oxidation step was observed. No acetophenone was observed, even at higher phosphite concentrations, therefore the reaction is purely ionic. These data indicate that other requirements for catalytic decomposition of hydroperoxide are sp^2 hybridized carbon atoms at positions 4 and 5 in the dioxaphospholane ring. The presence of a planar (e g. aromatic) ring is also of great importance. To demonstrate the antioxidant ability of the novel compound V, it was incorporated into polypropylene, and the ageing effects studied. (See chapter 8).

6.0 HYDROLYSIS OF CYCLIC PHOSPHATES

6.1 Introduction.

It has been shown that certain five membered cyclic phosphates hydrolyse at rates of greater than 1000 times that of their acyclic analogues[88]. With this in view, the hydrolysis of certain cyclic phosphates was briefly studied to see how this affects the hydroperoxide decomposition reactions. Workers have ascribed the antioxidant action of phosphites to the hydrolysis products[89], but in general it was found that water retarded the reactions studied. The work of Humphris and Scott[76] has shown that certain hydrolysis products from cyclic phosphate - hydroperoxide reactions, possess catalytic hydroperoxide decomposing activity.

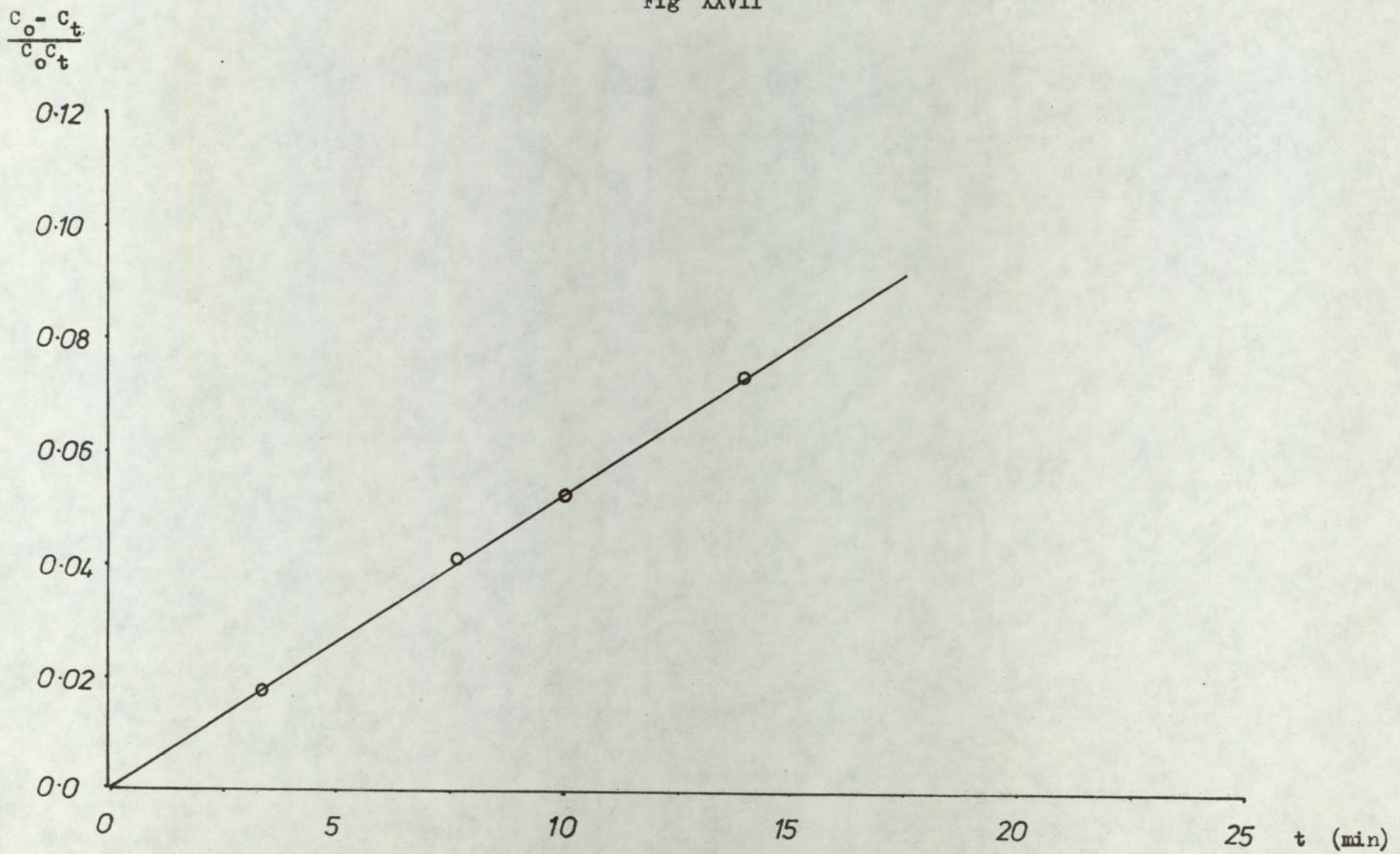
6.1.1 Results and discussion.

The reaction between C.H.P. and 2-oxo-2-hydroxy-1,3,2-dioxaphospholane was found to be dramatically retarded by traces of water. 1.0% of water caused the reaction rate to be approximately halved. The reaction of 2-oxo-2-hydroxy-1,3,2-dioxaphospholane with water was therefore studied. N.m.r. was used to follow the hydrolysis, the collapse of one of the methylene singlets was followed. Second order kinetics was observed, thus

$$-\frac{d[E.C.P.]}{dt} = k_2[E.C.P.][OH]$$

e.g. first order w.r.t. both reactants, using D.M.S.O_{d6} as solvent.

Fig XXVII



The hydrolysis of 2-hydroxy-2-oxo-1,3,2-dioxaphospholane in D.M.S.O. at room temperature

Cox, Wall and Westhiemer demonstrated strain in the 2-methoxy-2-oxo-1,3,2-dioxaphospholane ring by thermochemical measurements[88]; it was shown that the strain energy released in the formation of the transition state during saponification was responsible for the enhanced rate over the acyclic analogues.

The fact that five membered cyclic phosphates are hydrolysed faster than six membered rings and acyclic phosphates, led workers to study the ^{31}P n.m.r. spectra of various five membered cyclic phosphates[90]; less electron shielding of the phosphorus nucleus was found, which is consistent with diminuation of $d\pi - p\pi$ double bond character. Molecular orbital calculations carried out on strained five membered cyclic phosphates have shown that ring strain lowers the occupation of the phosphorus 3d orbitals[91]. The resulting deshielding results in a rapid rate of hydrolysis. This argument can be applied to the hydroperoxide decompositions, as the larger the deshielding effect at phosphorus, the greater is the chance of attack by hydroperoxide anion.

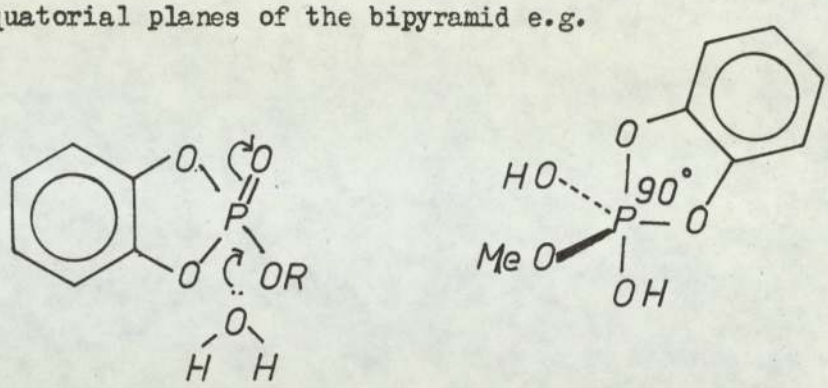
The hydrolysis of 2-chloro-2-oxo-1,3,2-dioxaphospholane was studied in T.H.F. It was shown that 2-hydroxy-2-oxo-1,3,2-dioxaphospholane was produced in high yield, and not the open chain analogue. This result can be explained on the basis of pseudo-rotation, if chlorine is placed favourably at the apex of the trigonal bipyramid intermediate, then it will leave as $Cl^{(-)}$;

only the cyclic phosphate will remain. Under basic conditions however, only ring opened products were obtained, because the intermediate oxanion, is too short lived to permit pseudorotation (91).

The hydrolysis of 2.6.4, 2.6.5, and 2.6.6, were investigated. Kinetic measurements wre attempted, using a variety of techniques including refractive index changes, U.V. spectroscopy and n.m.r. For isopropyl catechol phosphate, second order kinetics was observed, but the rates of hydrolysis compared with the aliphatic series were rapid. Products from the hydrolysis included alcohol (or phenol), o-hydroxyphenylphosphate, o-hydroxyphenyl alkyl phosphate, and catechol. The acid in products were isolated as their benzylthiuronium salts, and melting points taken. Paper chromatography showed that catechol was a product of all the phosphate hydrolysis reactions, despite reports to the contrary (91).

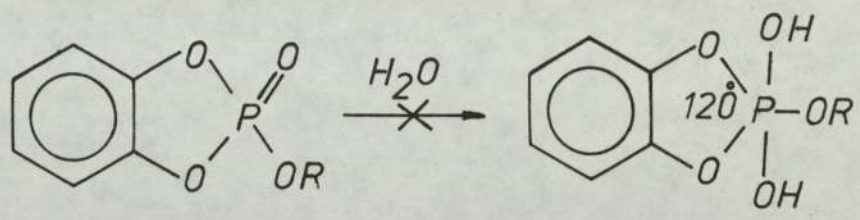
With limited quantities of water, 2-hydroxy-2-oxo-4,5-benzo-1,3,2-dioxaphospholane could be obtained as a hydrolysis product. This must arise from pseudorotation. The enhanced rate of hydrolysis of the five membered cyclic phosphates was discussed earlier, but the enhanced rate of ring retained hydrolysis, cannot be explained in terms of ring strain. Attack of water on 2-alkoxy-2-oxo-4,5-benzo-1,3,2-dioxaphospholane will lead to a penta-coordinate species free of ring strain because the ring O - R - O angle will have collapsed to 90° , and hence span the apex and

equatorial planes of the bipyramid e.g.



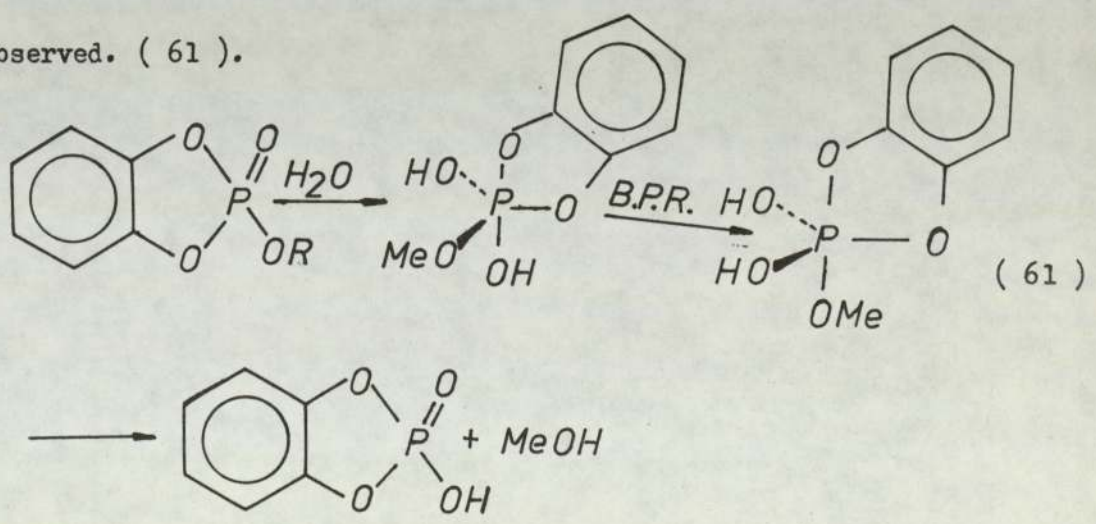
Ring span of the equatorial plane would be very unfavourable, since this angle is 120° , and a very strained system would result.

e.g. (60).



(60)

Hence with limited quantities of water the following mechanism was observed. (61).

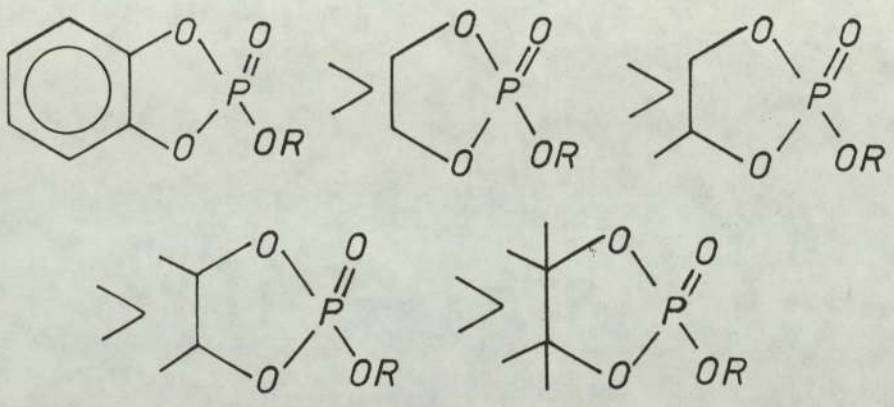


(61)

Under alkaline conditions however, only ring opened products were obtained in agreement with studies by Kaiser et al.[92] .

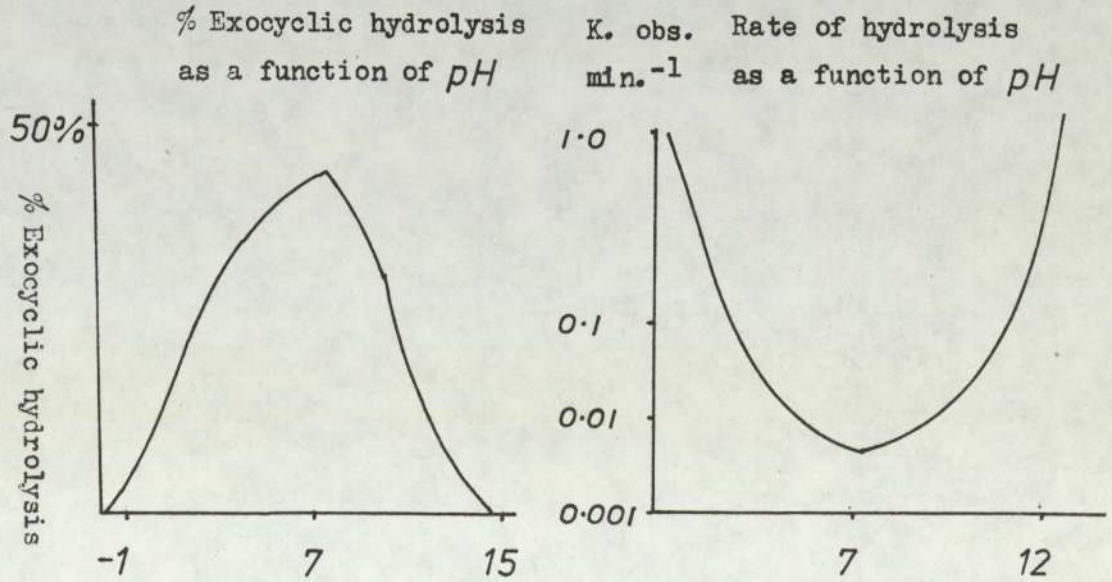
It has been shown that stepwise replacement of the hydrogens in the dioxaphospholane ring stabilizes the ring toward hydrolysis. The study agrees with work by Edmundson on 2-thiono-1,3,2-dioxaphospholane rings[93]. The effects were thought to be electronic rather than steric[93].

From this study the following generalizations can be drawn for the rates of reaction of water with cyclic phosphates. (62).



(62)

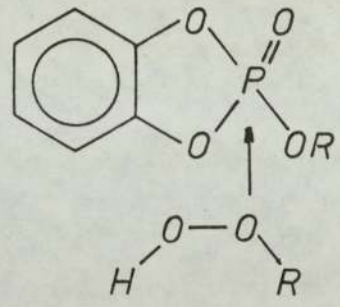
The following graphs by Westheimer[101] are in agreement with the hydrolysis effects found in this laboratory.



7.0 SOME APPLICATIONS OF THE CYCLIC PHOSPHATE / HYDROPEROXIDE REACTION

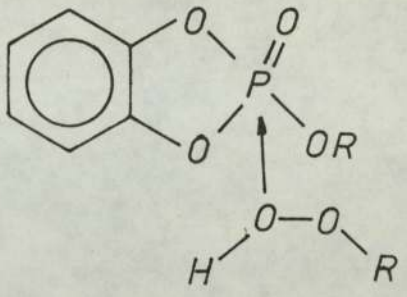
7.1 Epoxidation reactions. Introduction.

In view of the fact that cyclic phosphate esters based on catechol, have the ability to decompose diaralkyl and dialkyl peroxides by an ionic mechanism; the possibility was thought to exist for the coordination of the hydroperoxy alkyl oxygen to phosphorus. e.g. for cumene hydroperoxide.



(g)

instead of



(h)

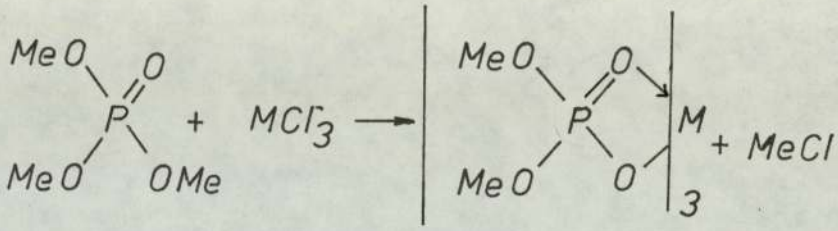
If (g) occurred then electrons would tend to be drawn from the hydroperoxy oxygen (h) and present a potential species for epoxidation reactions. Analogous observations have been made for certain boron compounds[94][95].

7.1.1 Results.

It was found that cyclic phosphate esters based on catechol decomposed cumene hydroperoxide in various olefins with the formation of mainly phenol and acetone. Very small quantities of epoxide

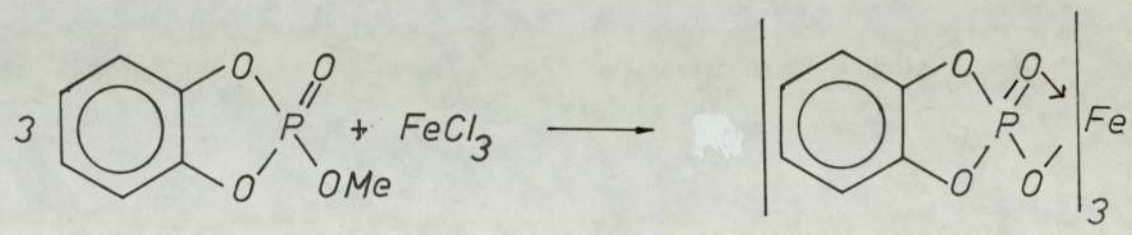
were formed, and hence it was shown that the cyclic phosphates were not catalysts for epoxidation, at the concentrations tested. (1 : 1000, 1 : 100, 1 : 10).

It was therefore decided to prepare a series of metal chelates, derived from catechol cyclic phosphates. Phosphato chelates have been prepared by the reaction of trimethylphosphate with anhydrous metal halides[96] (63).

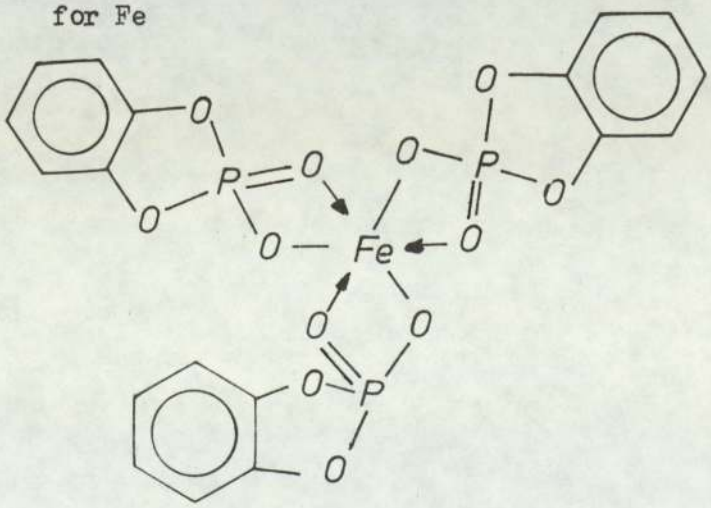


(63)

The reaction of anhydrous ferric chloride with 2-methoxy-2-oxo-4,5-benzo-1,3,2-dioxaphospholane gave high yields of the iron III chelate,



an analogous vanadium compound was prepared. I.R. studies indicate that the complexes are octahedral, (no free OH) e.g. for Fe

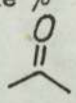
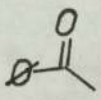
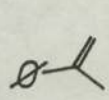
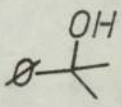


The structure of the molybdenum complex is uncertain.

The reaction of the novel metal complexes with cumene hydroperoxide was investigated in chlorobenzene. The molybdenum, and iron complexes decomposed C.H.P yielding the ionic products phenol and acetone. Table XIX shows the product distribution for the reaction between C.H.P. and a catalytic amount of the catechol phosphate, metal phosphate complexes and C.H.P. in chlorobenzene.

Table XIX

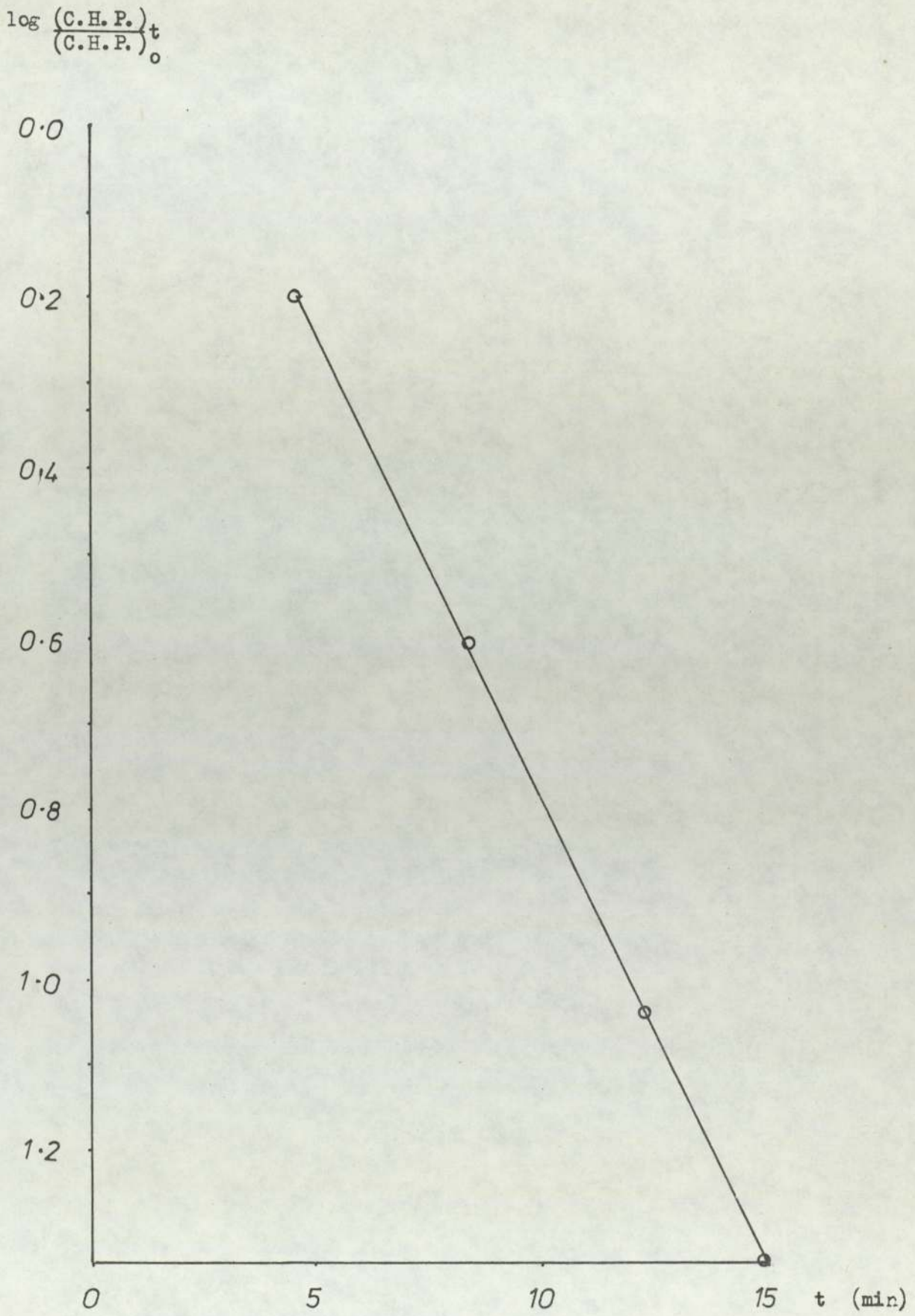
Product distribution for decomposition of C.H.P. using metal complexes in chlorobenzene at 75 C. mole %

Complex	Temp.	$\frac{(CHP)}{(complex)}$	ØOH				
Fe	75°C.	10	88.2	57.3	2.0	-	-
Mo	75°C.	10	79.6	60.0	1.5	-	-
V	75°C.	10	55.2	38.1	14.0	20.8	46.2

The vanadium complex however, gave a mixture of ionic and free radical decomposition products. The iron and molybdenum complexes proved to be very good catalysts for the decomposition of C.H.P. following pseudo first order kinetics. (Fig. XXVIII). The iron complex gave a first order rate constant of 4.94×10^{-3} sec.$^{-1}$, the molybdenum catalyst was a more efficient peroxide decomposer, $K_1 = 4 \times 10^{-2}$ sec.$^{-1}$.

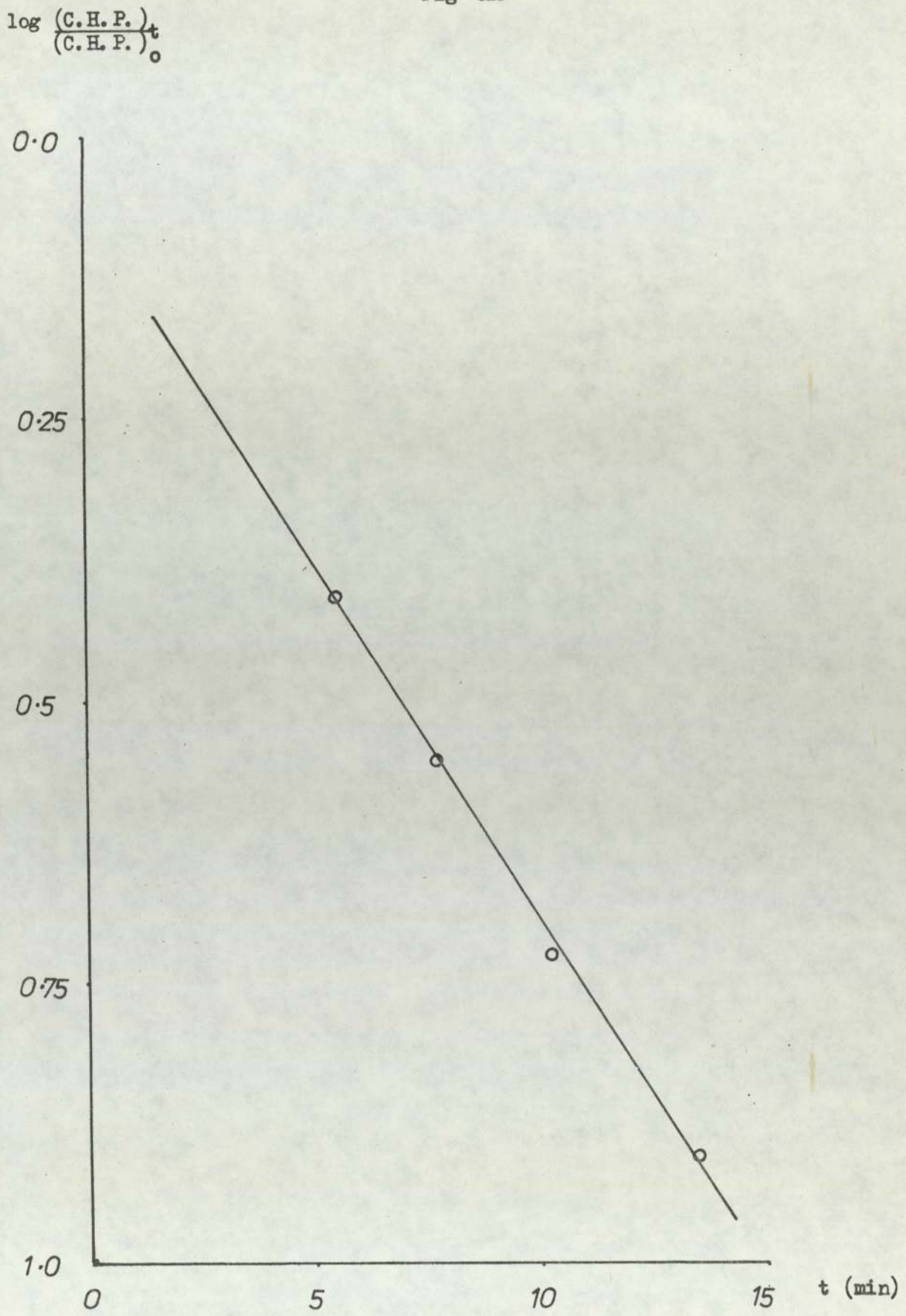
The metal chelates studied were found to be excellent

Fig XIX



The decomposition of C.H.P. (0.1 mole) using 2.7.1. (0.01 mole) in chlorobenzene at 75°C

Fig XX



The epoxidation of cyclohexene followed by the decomposition of C.H.P. (0.1 mole) using 2.7.3. at 75°C in ØCl

catalysts for the epoxidation of olefins (with the exception of iron). Catalyst / hydroperoxide ratios of greater than 1 : 1000 were found to give quantitative amounts of cyclohexene epoxide from cyclohexene. Dodecene gave quantitative yields of dodecene epoxide.

The kinetics of epoxidation were studied using pure cyclohexene, and the molybdenum and vanadium chelates were found to give first order kinetics, when cyclohexene was used as the solvent, but second order kinetics was observed when the epoxidation was carried out in an inert solvent, using equimolar amounts of C.H.P. and cyclohexene. The kinetics of epoxidation using excess olefin were found generally to be of first order. The rate constant for the epoxidation of cyclohexene using the molybdenum chelate at 1 : 100 catalyst to C.H.P. ratio was found to be 2.93×10^{-3} sec.$^{-1}$.

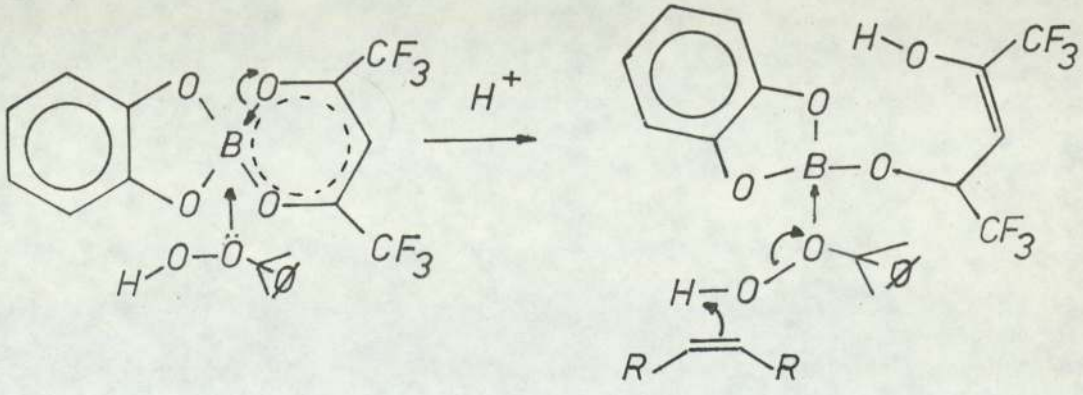
The reaction of oct-1-ene with C.H.P. and molybdenum catalyst was carried out in nitrogen and in oxygen. The rate difference was small e.g. with ± 5%, and hence the mechanism was shown to be ionic rather than free radical. The following table shows epoxide yields based on hydroperoxide conversion for various olefins.

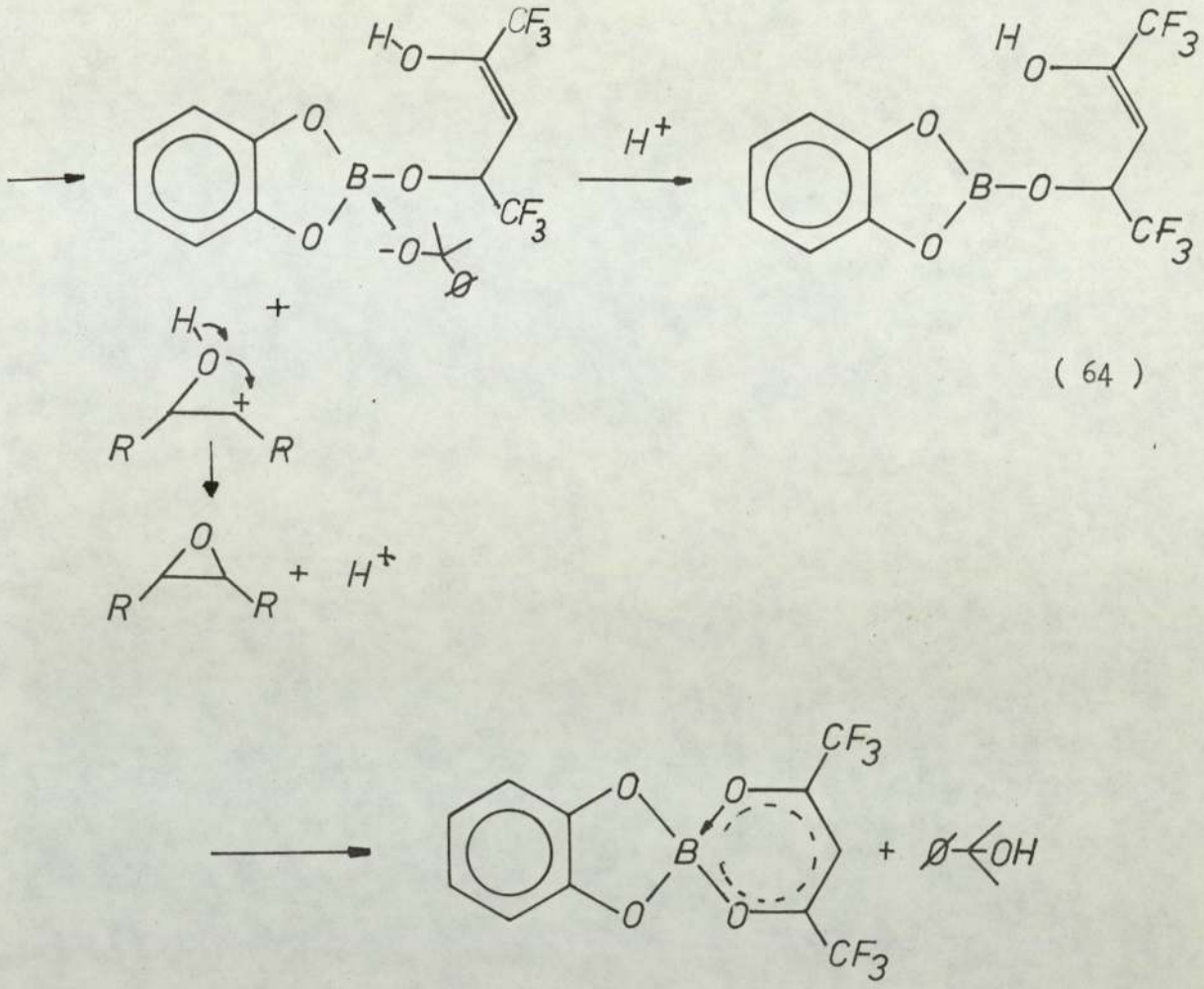
Hydroperoxide	Olefin	Temp.	Yield epoxide
C.H.P.	cyclohexene	75°C.	89%
C.H.P.	dodec-1-ene	75°C.	92%
C.H.P.	oct-1-ene	75°C.	95%

The catalytic effect was found to be retarded after the metal chelate had been exposed to air. Hence all manipulations involving the metal chelates were performed in a glove bag under dry nitrogen.

7.1.2 Discussion.

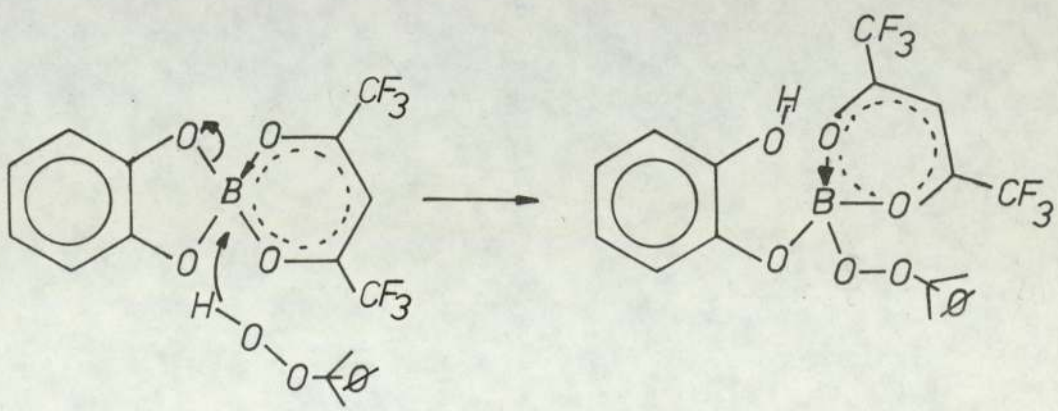
It was shown in 7.1.1 that cyclic phosphate esters based on catechol were not efficient catalysts for the epoxidation of olefins. The attack of the hydroperoxy anion at phosphorus is faster than coordination of the peroxy alkyl oxygen, even in olefin solution. However Lewis acid strength has been associated with epoxidation ability in certain boron complexes[95]. The acetylacetone and hexafluoroacetylacetone complexes of o-phenylene boronate were tested as epoxidation catalysts by Sheldon et al.[95] and it was shown that the hexafluoroacetylacetonate was an efficient epoxidation catalyst. Recent work in this laboratory[96] has shown that the acetylacetonate complex is not a catalyst for hydroperoxide decomposition, whereas the hexafluoroacetylacetonate complex is a hydroperoxide decomposer. Two mechanisms can be used to explain these results; if the alkyloxy oxygen of the hydroperoxide can coordinate with boron in the presence of an olefin, the trifluoromethyl group is such a strong electron withdrawing group that the Lewis base electrons of the ligand may be displaced e.g. (64).

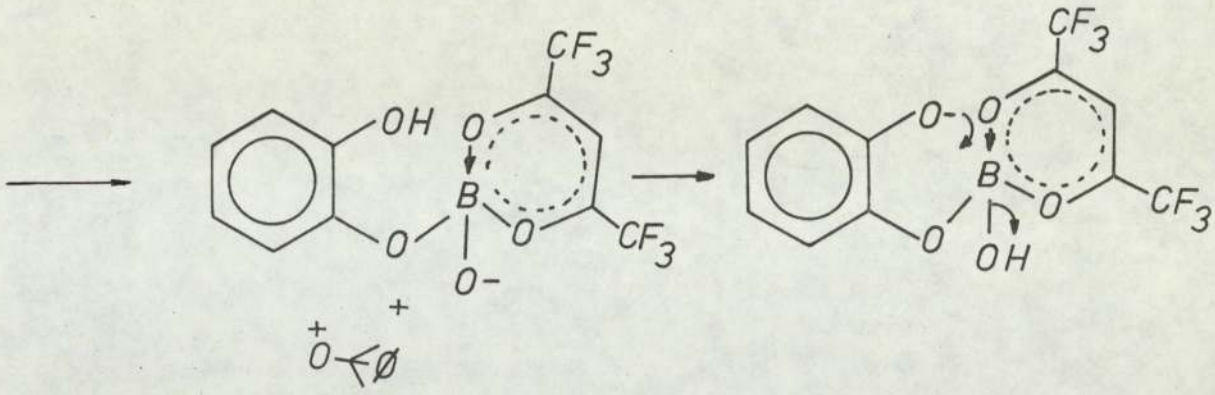




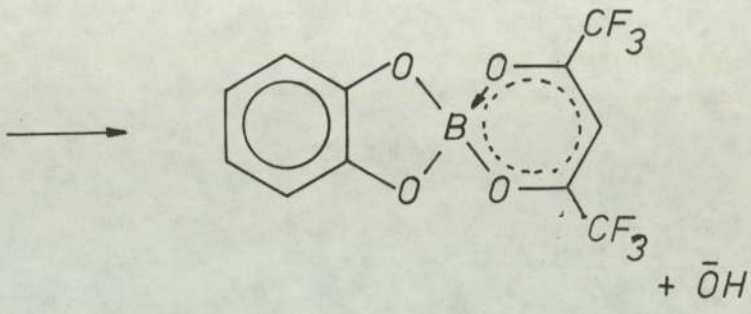
(64)

Thus the empty p-orbital on boron may be responsible for the epoxidation mechanism. The hydroperoxide decomposition could involve ring opening, and thus ring strain (as observed in the phosphorus series) may be involved in the mechanism (65) by a direct SN_2 attack on boron.





(65)



In both mechanisms the catalyst is regenerated.

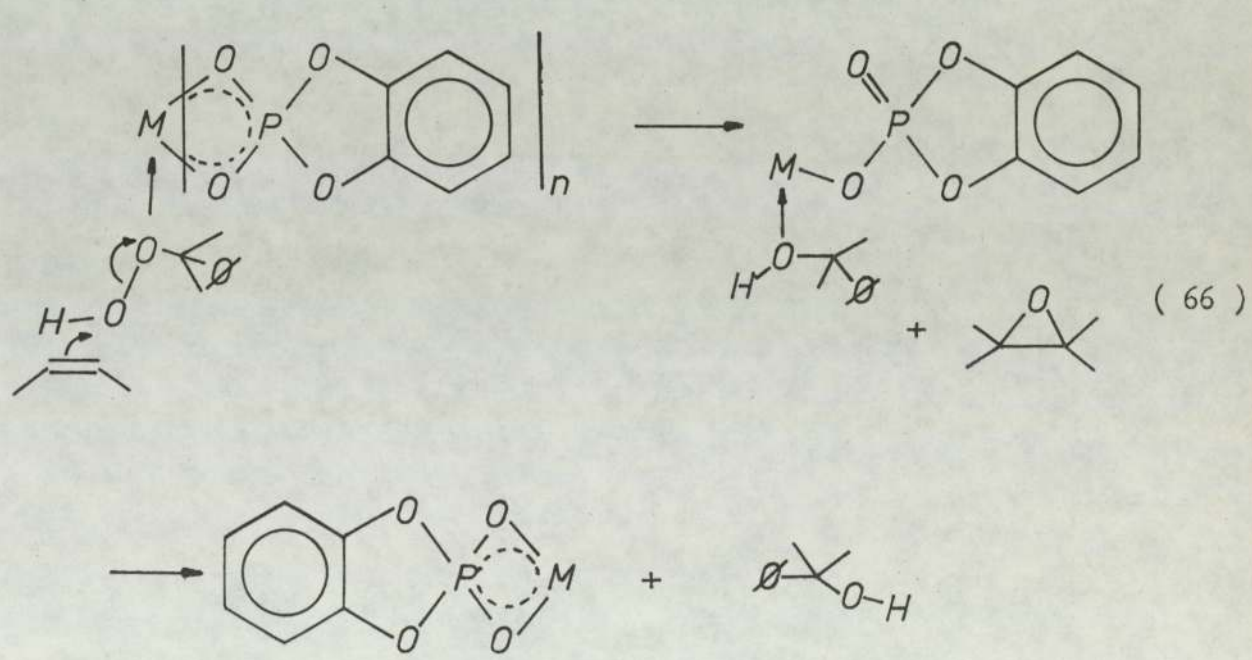
Metal chelates were prepared with the view to preventing attack of perhydroxyl ion at phosphorus, and increasing the chance of alkyloxy oxygen coordination (see 66 and 67). The molybdenum and vanadium chelates proved to be excellent catalysts for epoxidation, and were more efficient than molybdenum hexacarbonyl induced epoxidation[97] or boric oxide induced epoxidation[71]. The kinetics of epoxidation were found to be second order, in chlorobenzene, and first order w.r.t. each reactant thus

$$\frac{-d(CHP)}{dt} = K_2(CHP)(olefin)(chelate)$$

where (chelate) is a true catalyst for the reaction.

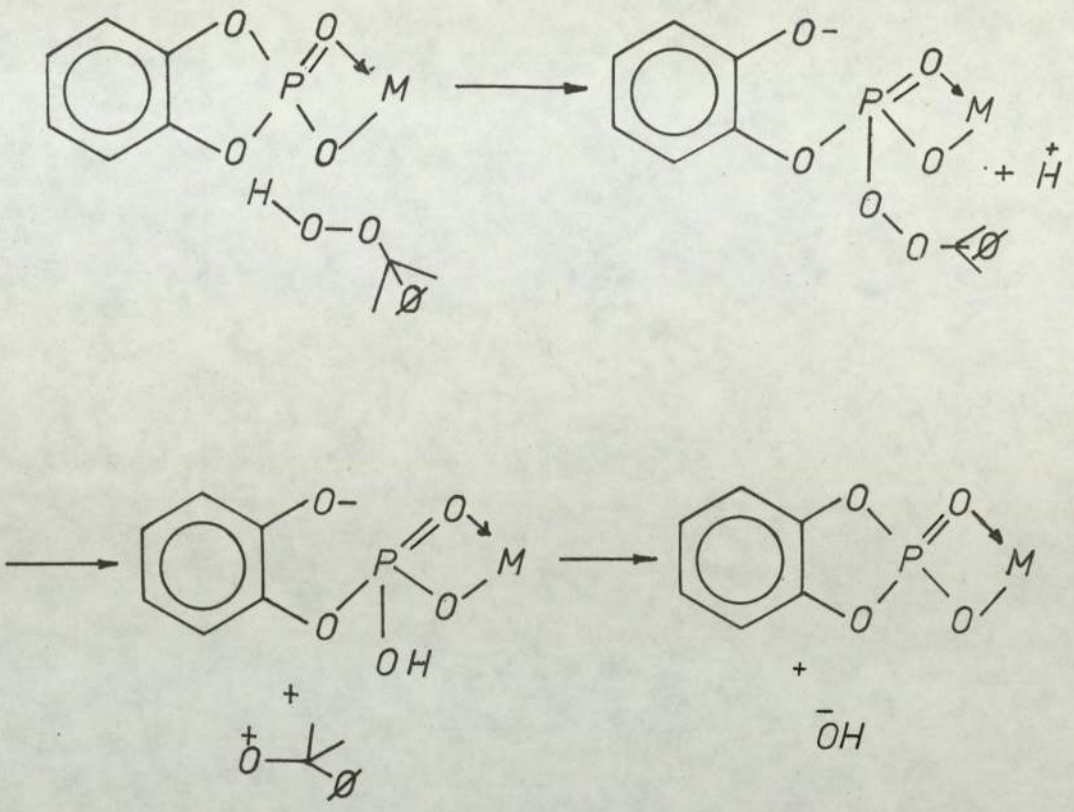
The mechanism of epoxidation was found to be ionic as shown in 7.1.1, faster reaction times were observed with cyclohexene than oct-1-ene. Qualitative tests showed methylcyclohexene to react even faster, thus the mechanism should involve electrophilic attack of oxygen on the double bond. The presence of a +I group forms an electron rich centre for electrophilic attack, conversely, the less +I groups the slower the reaction.

Coordination of the hydroperoxide with either the metal or phosphorus is possible; this may explain the efficiency of these compounds as catalysts for epoxidation. The reaction scheme below is consistent with the observed facts. (66).

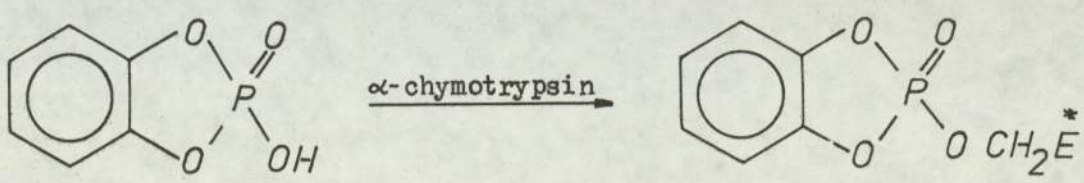


(66)

In solvents inert to epoxidation e.g. ØCl, the following mechanism could occur (67).



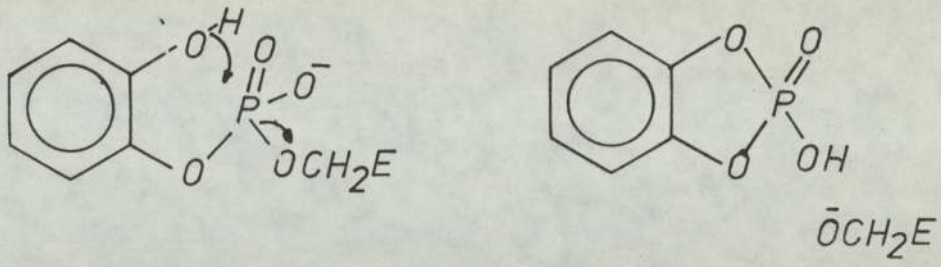
The regeneration of the cyclic phosphate is similar to that observed in certain enzyme reactions[98]. Catechol cyclic phosphate reacts stoichiometrically with α-chymotrypsin at ph 6.98 at 25°C. to form j[99][100].



(i) (j)

* E = Enzyme

The phenolic hydroxyl group in (j) was found to act as an intramolecular nucleophile attacking phosphorus with a first order rate constant of 3.8×10^{-4} sec.$^{-1}$. The pseudo first order rate constant for the attack of water on (j) was found to be 3.5×10^{-7} sec.$^{-1}$. The proximity effect of the phenolic hydroxyl as shown by X ray crystallography[98], was shown to be responsible for ring closure, even though this involves the formation of a highly strained five membered ring. (68).

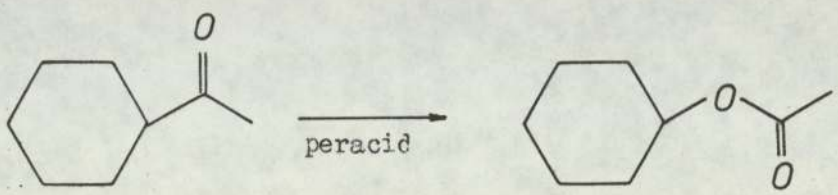


(68)

7.2 Baeyer Villiger Reactions.

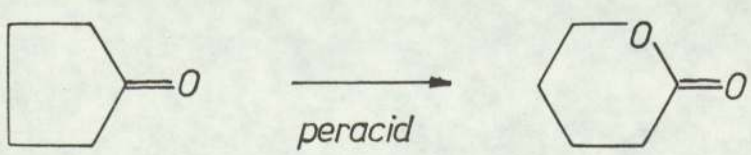
7.2.1 Results and discussion.

The reaction of ketones with peracids was investigated by Baeyer in 1898[102][103]. It was shown that the peracid oxidation of aromatic, cycloalkyl, and aliphatic ketones with the carbonyl group attached to at least one secondary atom, gave esters (69).



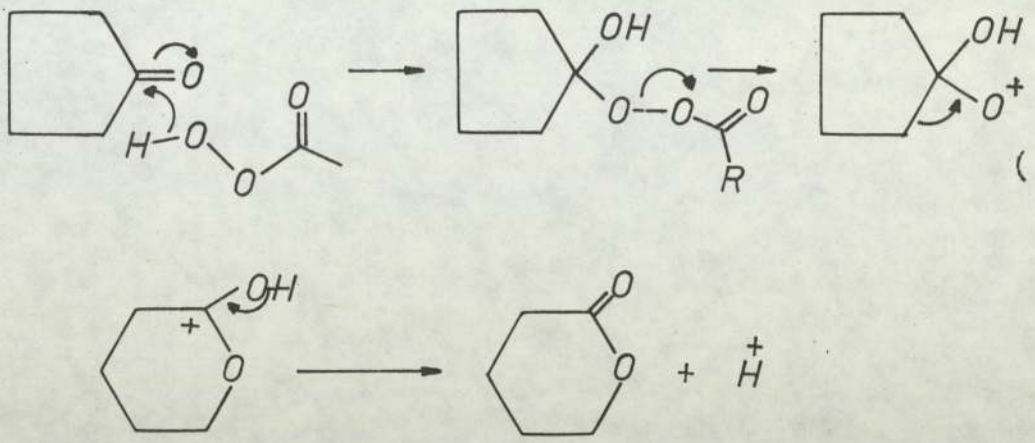
(69)

Cyclic ketones were found to yield lactones[104][105][106]. (70)



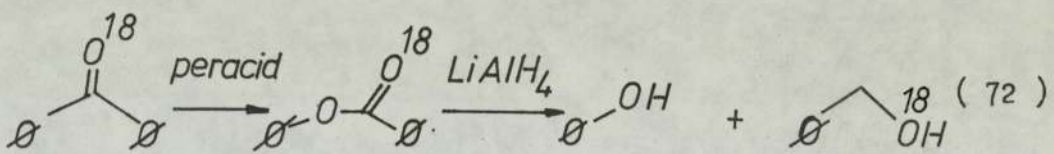
(70)

Criegee in 1948 postulated the following mechanism as illustrated by the oxidation of cyclopentanone. (71).



(71)

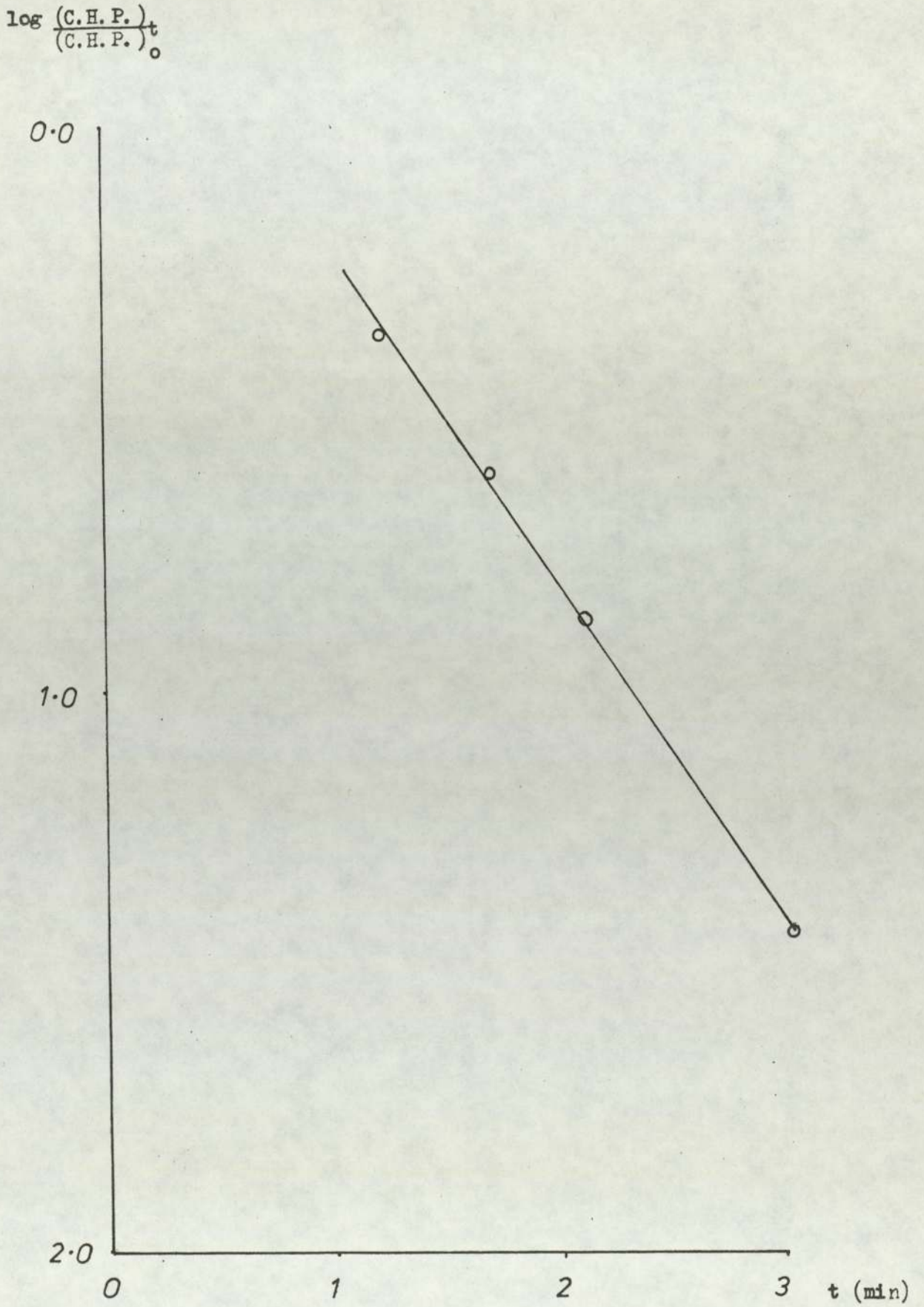
Doering[107] supported this mechanism by O^{18} labelling reactions; it was shown that benzophenone O^{18} was completely retained in Baeyer Villiger reactions. (72).



(72)

In view of their catalytic epoxidation activity, the metal chelates 2.7.1, 2.7.2 and 2.7.3, were studied as Baeyer Villiger catalysts. The vanadium chelate showed the greatest activity. The main products from a reaction carried out in cyclohexanone using various ratios of C.H.P. to 2.7.2 were phenol and acetone; only 4.0 mole % of caprolactone was produced. This is most certainly due to the electrophilic nature of the hydroperoxy oxygen. For the Baeyer Villiger reaction an electron rich centre is required to attack the carbonyl of the ketone. In view of the electrophilic nature of the

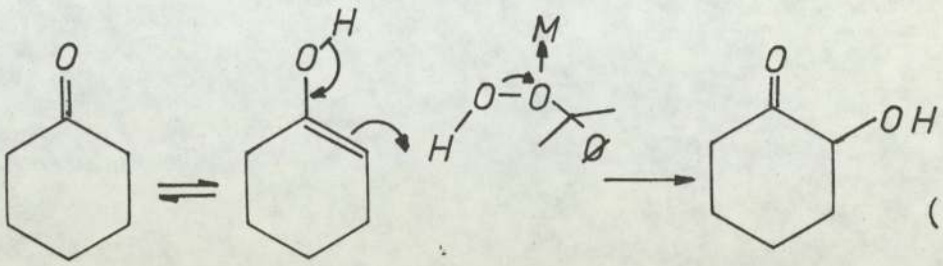
Fig XXI



The decomposition of C.H.P. (0.1 mole) using 2.7.2.(0.01 mole)

in cyclohexanone at 75°C

hydroperoxide / metal complex system, the following mechanism was thought possible with ketones. (73).



(73)

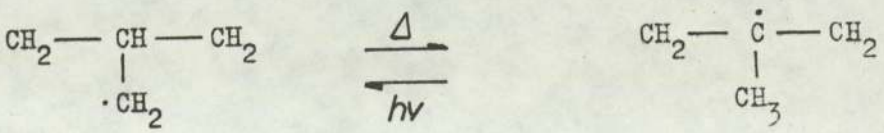
e.g. acyloin formation. Further work is required in this field.

8.0 POLYMER STUDIES

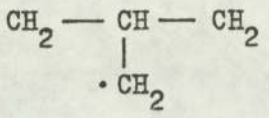
8.1 Introduction.

2-(3-Hydroxynaphthyloxy)-4,5-naphtho-1,3,2-dioxaphospholane was shown to be a very effective catalyst for hydroperoxide decomposition (chapter 5). The compound was therefore incorporated into a polymer, to study the antioxidant activity. Polypropylene was chosen as a suitable polymer, as it is easily degraded by light (108). The ease of degradation has been attributed to the labile tertiary hydrogen atom present in each polypropylene unit. Although the pure polymer should be inert towards sunlight, hydroperoxides are formed as a result of heat treatment during processing. The hydroperoxide can act as an initiator for the photooxidation of polypropylene, as the quantum efficiency for polypropylene hydroperoxide photolysis is approximately unity (109).

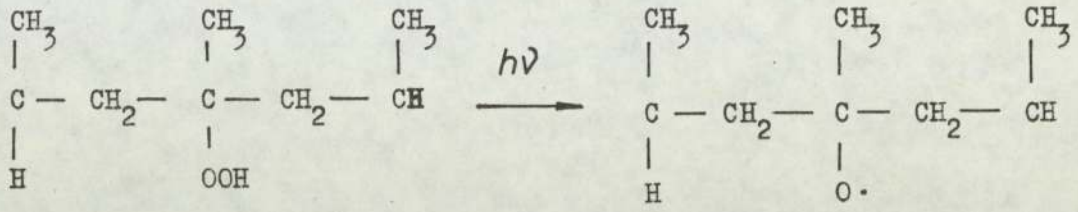
The E.S.R. spectrum of U.V. degraded polypropylene was investigated by Tsuji et al. (110). These workers found that when an irradiated polymer sample was allowed to stand in the dark for several days at -196 C., an eight line E.S.R. spectrum was produced; this reverted to a four line spectrum after re-irradiation. This is consistent with the following scheme.



The spectrum after photolysis was attributed to methyl and

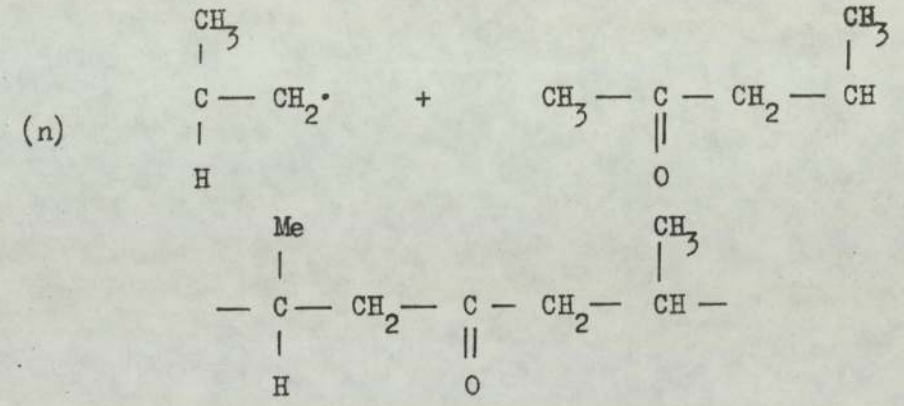
 radicals.

The mechanism of radical formation was thought to be homolysis of the initially formed hydroperoxide[113], (m).



(m) (n)

followed by secondary decomposition of the precursor alkoxy radical (n).



The ketones formed can undergo photolysis to produce radicals or unsaturated moiety, by Norrish I and II mechanisms respectively[111]. Trozzolo and Winslow[112] have suggested that triplet carbonyl, formed by the photolysis of singlet carbonyl, can react with triplet oxygen, to give singlet oxygen. The singlet oxygen could react with unsaturation in the polymer to give allylic hydroperoxide, which could then photolyse to continue the degradation.

It has been shown that although aromatic ketones are effective photoinitiators, long chain aliphatic ketones do not possess this

property [114], so that the above statement about triplet carbonyl sensitization of O_2 would seem incorrect. It has also been shown that polypropylene subjected to photo oxidation during processing suffers a considerable reduction in U.V. lifetime before the formation of carbonyl [115].

8.2 Techniques.

The antioxidant samples were mixed with unstabilized polypropylene powder, and the mixtures were heated in a torque rheometer at 180°C. for 5 minutes under an atmosphere of argon. The samples were rapidly removed and placed in cold water. The cooled samples were dried and preserved in polythene bags under nitrogen. Each sample (~ 10g.) was pressed into a film at 180°C. between photographic glazing plates. The plates were maintained at 180°C. for 2 minutes, and cooled to 60°C. before removing the polypropylene films from the press.

Samples of polypropylene of constant thickness were cut from the prepared sheets and mounted on cardboard of suitable size, for infra-red measurements. The mounted polypropylene samples were subjected to photodegradation in a U.V. cabinet, and the I.R. spectrum of each was recorded at set time intervals. The carbonyl index of polypropylene was measured, and plotted as a function of time.

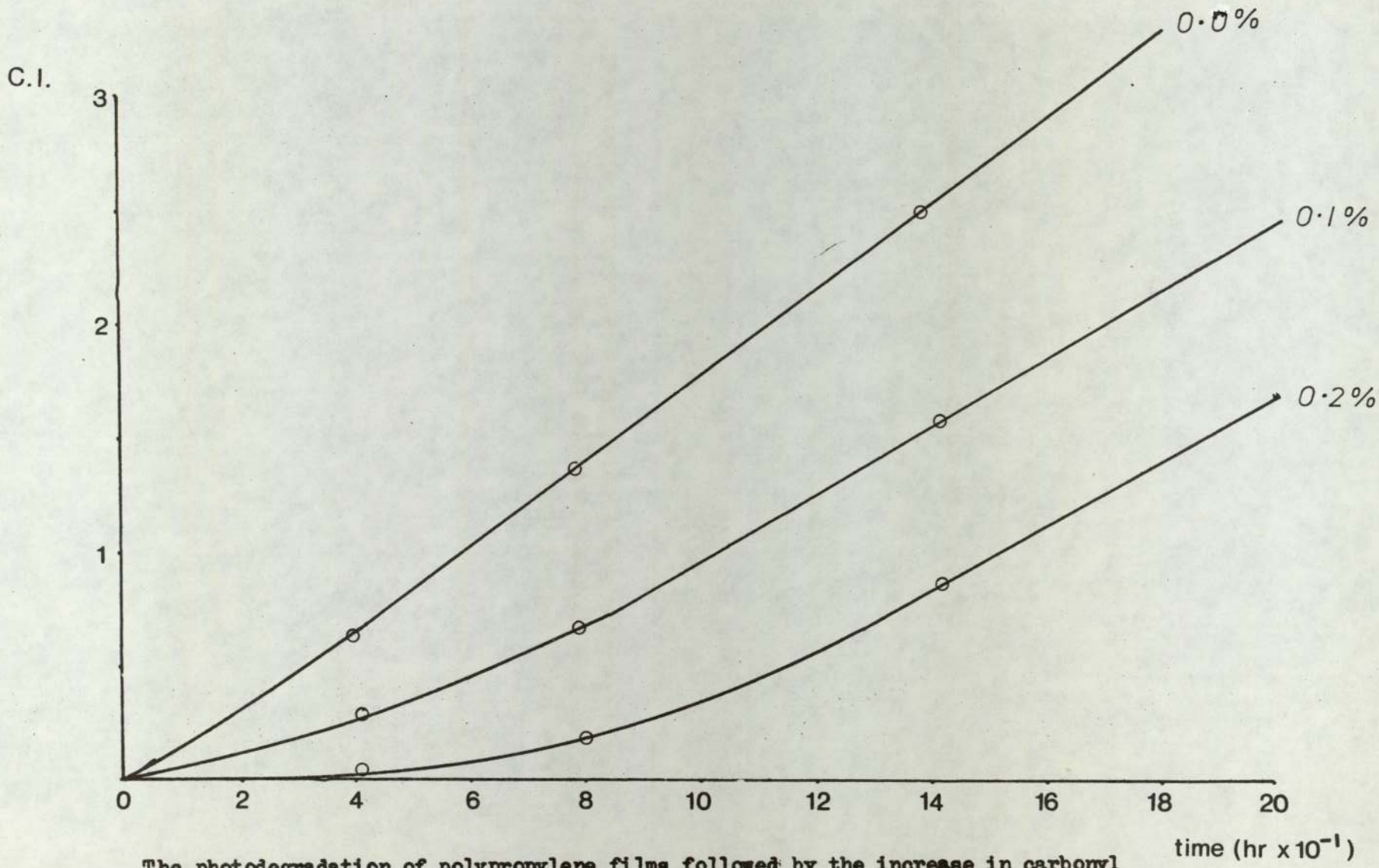
$$\text{Carbonyl index} = \frac{1710\text{cm}^{-1}}{2720\text{cm}^{-1}}$$

8.3 Results and discussion.

Plots of carbonyl index versus time for a variety of antioxidant concentrations are shown overleaf. The shapes of the graphs obtained are interesting. Unstabilized polypropylene shows an initial slow increase in carbonyl followed by a steady rate of oxidation, with an embrittlement time of only 40 hr. Polypropylene stabilized with 0.1% 2-(3-hydroxynaphthyloxy)-4,5-naphtho-1,3,2-dioxaphospholane shows a much slower initial carbonyl growth rate, followed by a steady but slower rate of oxidation compared with unstabilized polypropylene; the embrittlement time observed was ca 120 hr. Polypropylene stabilized with 0.2% 2-(3-hydroxynaphthyloxy)-4,5-naphtho-1,3,2-dioxaphospholane shows an even slower initial carbonyl formation (120 hr.), followed by a steady rate of oxidation, which is comparable with the 0.1% stabilized sample. These data indicate that a species is formed after the initial oxidation period, which retards the oxidation rate, compared with the unstabilized sample. As no carbonyl was observed in a sample containing antioxidant which was processed in air, the compound is probably a thermal stabilizer.

Results by Humphris and Scott (116) have shown that 2-(2,6-di-t-butyl-4-methylphenoxy)-2-oxo-1,3,2-dioxaphospholane is an effective heat stabilizer in polypropylene. The induction period to carbonyl formation with 0.2% antioxidant was shown to be 170 hr.

Fig XXII



The photodegradation of polypropylene films followed by the increase in carbonyl index

at 150° C. As U.V. radiation is more effective in cleaving hydroperoxides than thermolysis (e.g. for 100 - 150° C.). The naphthalene phosphite and phosphate systems may be more effective stabilizers than the catechol phosphates. The following table summarizes the induction periods and embrittlement times for the photodegradation of polypropylene stabilized with 2-(3-hydroxynaphthyloxy)-4,5-naphtho-1,3,2-dioxaphospholane.

Time for steady oxidation rate hr.	Embrittlement Time hr.	% antioxidant
45	45 - 50	0
90	120	0.1
120	175	0.2

The antioxidant did not colour the polypropylene samples, but during photodegradation, the polymer went slightly opaque when the constant rate oxidation stage was reached.

9.0 CONCLUSIONS

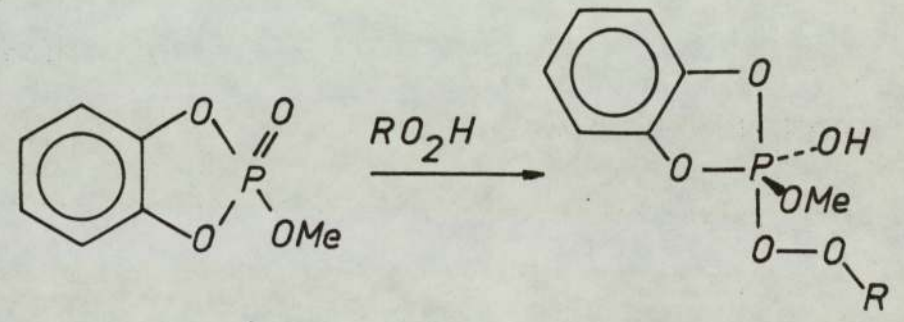
It has been shown that five membered cyclic phosphate esters react with hydroperoxides to give a variety of decomposition products, whereas the simple acyclic alkyl and aryl phosphates are not peroxide decomposers. Unsubstituted aliphatic cyclic phosphates were shown to react stoichiometrically with hydroperoxides, by an ionic mechanism.

Replacement of the hydrogen atoms in the dioxaphospholane ring by methyl groups, retarded the reaction rate and changed the mechanism of the hydroperoxide decomposition; a free radical reaction was observed. The aromatic cyclic phosphate esters were powerful peroxide decomposers, reacting with both hydroperoxides and peroxides catalytically, by an ionic mechanism; thus various factors seem important in the catalytic process.

The presence of a five membered ring and hence the influence of ring strain is important, because the six membered ring is strain free and inert towards hydroperoxide. The five membered strained ring reduces the phosphorus d orbital occupation and $d\pi - p\pi$ bonding is also altered as the geometry of the phosphate is forced to a distorted tetrahedron. In six membered rings, the phosphate assumes a normal tetrahedral array. These facts show that in five membered rings, phosphorus is relatively deshielded, and in a highly reactive state toward nucleophiles including hydroperoxide.

The aliphatic series were not true catalysts for hydroperoxide decomposition due to the tendency of these compounds to polymerize; the sp^3 carbon atoms in the dioxaphospholane ring were readily attacked by nucleophiles. The carbon atoms in the aromatic phosphate esters are sp^2 hybridized and nucleophilic attack on these was not observed.

Apart from ring strain resulting in deshielding at phosphorus, the five membered rings are hydrolysed by an exclusive mechanism involving pseudorotation. The intermediate pentacoordinate phosphorus species is strain free, and hence the driving force for the reaction with hydroperoxide will be partly due to this phenomenon.



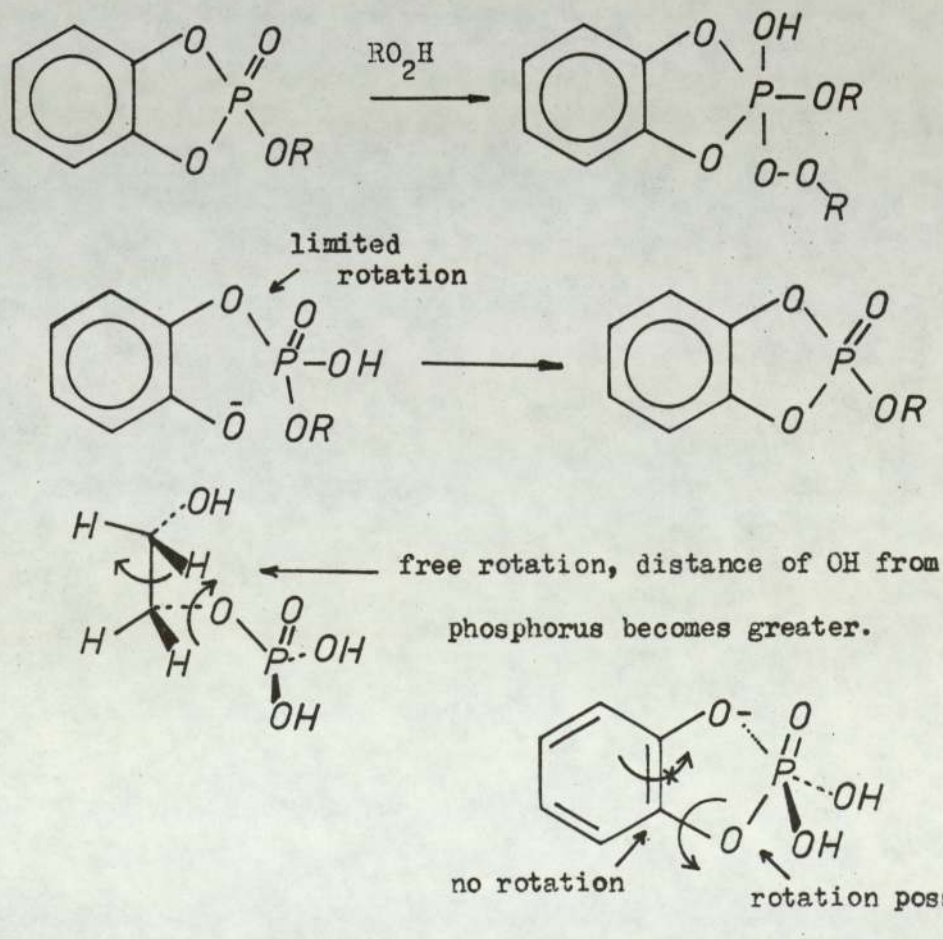
strained no strain

This mechanism is not observed for six membered rings in hydrolysis reactions; a square pyramidal transition state is obtained with the leaving group at the apex.

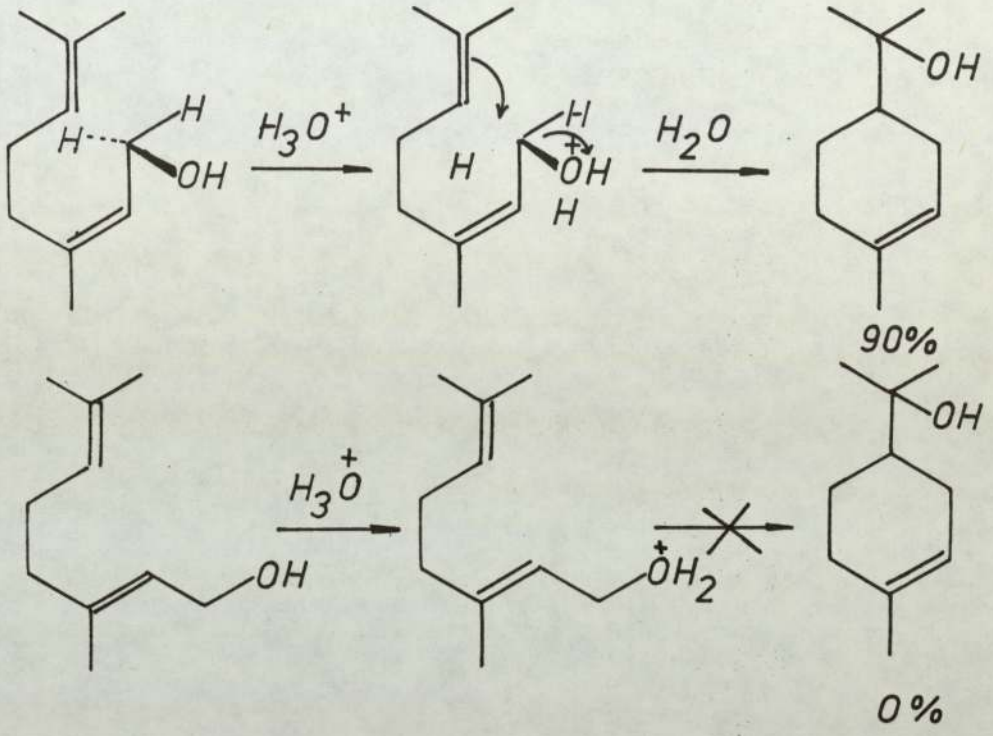
Substitution of the hydrogen atoms in ethylene cyclic phosphate with methyl groups alters the rate of reaction with cumene hydroperoxide by virtue of steric effects. The +I nature of the methyl groups may result in electron donation to the phosphorus

atom, thereby reducing the ionic nature of the peroxy bond; thus explaining the free radical decomposition observed. The order of stability of the t-butyl cyclic phosphates is in agreement with the above observations.

Increasing the conjugation in the aromatic ring of catechol cyclic phosphate esters was also found to enhance peroxide decomposing ability. The increasing conjugation must therefore result in greater deshielding of the phosphorus atom. Another interesting observation is that the aromatic hydroxyl in aryl cyclic phosphates is not as free to rotate as the aliphatic hydroxyl. This may result in a neighbouring group effect and contribute to the catalytic peroxide decomposing ability, by a similar mechanism to that observed in the enzyme systems (see chapter 7).

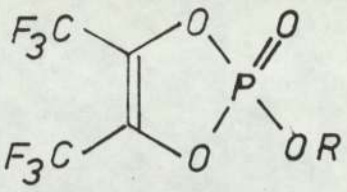


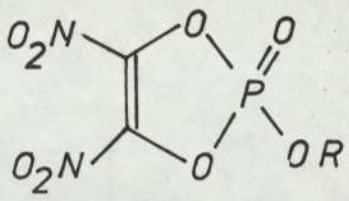
The arguments of distance affecting reactivity are clearly shown in the cyclization of nerol and geraniol in acid media. The cis isomer (nerol) will undergo ring closure in the presence of acid.



The trans isomer (geraniol) will not cyclize. Acyclic phosphates containing suitable electron withdrawing groups should also be effective peroxide decomposers as the shielding at phosphorus will be lowered. The tris-trimethylsilyl phosphates have been shown to decompose hydroperoxide. This must be due to vacant silicon d orbitals overlapping filled oxygen p orbitals and thus withdrawing electrons from oxygen; this lowers the shielding of phosphorus and thus enhances reactivity toward hydroperoxide. These arguments are consistent with the observed facts.

Thus

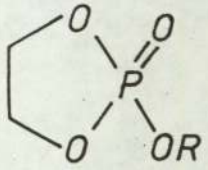
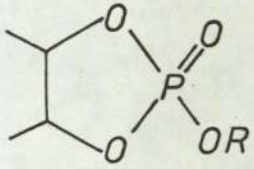
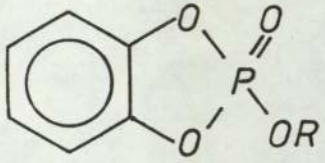
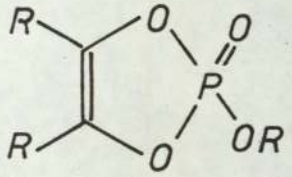
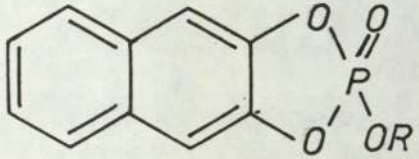
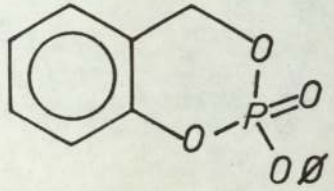




should be powerful peroxide decomposers.

The following table summarizes the features of cyclic and other phosphates possessing peroxide decomposing ability.

Table XX

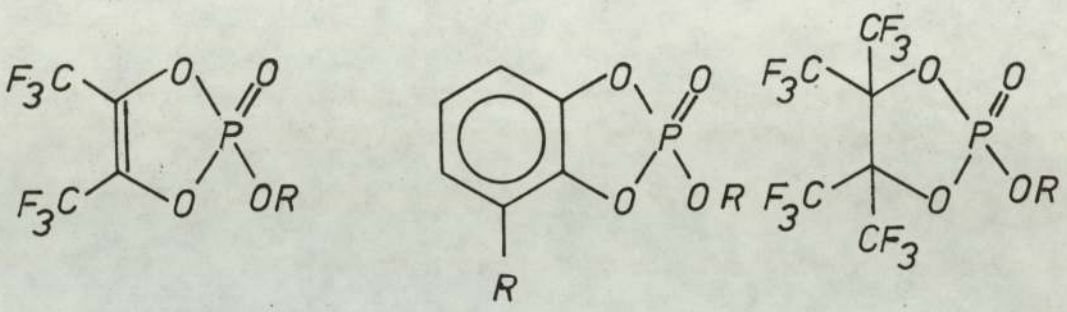
Cyclic Phosphate	Structural Features	Reaction with Hydroperoxide	Mechanism
	Strained ring. No ring substituents R=H or alkyl, sp^3 carbon	ca stoichiometric	ionic
	+I Me substituents in ring P shielded R=phenyl sp^3 carbon	very weak catalyst	free radical
	Aromatic ring fused to dioxaphospholane system. sp^2 carbon atoms R= alkyl or aryl strained ring	powerful decomposer, very strong catalyst	ionic
	sp^2 carbon atoms strained ring	very weak catalyst	R=Me free radical
	sp^2 carbon atoms strained ring	very powerful catalyst	ionic
	6 membered ring, no strain chain conformation	inert	----
$(Me_3SiO)_3PO_4$	Si d orbitals overlap O p orbitals	decomposer	----

The metal chelates derived from catechol cyclic phosphate esters proved to be efficient peroxide decomposers, and the vanadium and molybdenum compounds catalysed the epoxidation of olefins. Attempted Baeyer Villiger reactions catalysed by the complexes were not successful. This is probably due to the electrophilic nature of the peroxy oxygen (shown by the enhanced rate of epoxidation of +I substituted olefins). The synergic effect of the metal - ligand bonds may be an important feature of the ability of these complexes to both catalyse epoxidation and destroy hydroperoxide, by shielding the phosphorus, and thus only allowing loose coordination to hydroperoxide.

Finally polymer studies with the novel naphthalene phosphite showed that the compound was an effective antioxidant in polypropylene. The phosphite did not colour the polymer, and this would be advantageous in colourless materials. Secondly, the antioxidant did not hydrolyse rapidly or become sticky in air, as did the catechol derivatives. The material is virtually odourless and can be weighed in air.

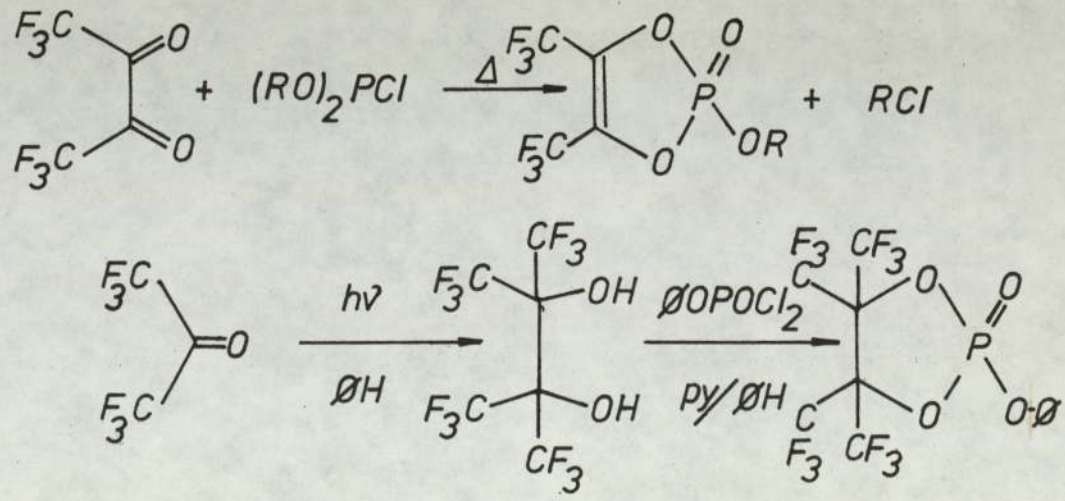
10.0 SUGGESTIONS FOR FURTHER WORK

From the foregoing discussion it was concluded that ring strain, and the presence of suitable electron withdrawing groups in five membered cyclic phosphates, are essential features of their peroxide decomposing ability. It would therefore seem pertinent to synthesize the following compounds:



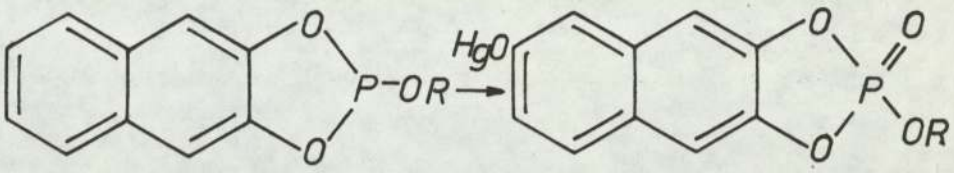
R=Me, Bu^t, CF_3

The following routes are suggested:

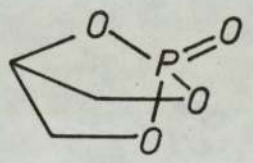


Studies on the naphthalene series are also important, as these may impart considerable stability to polymer systems. As phosphites

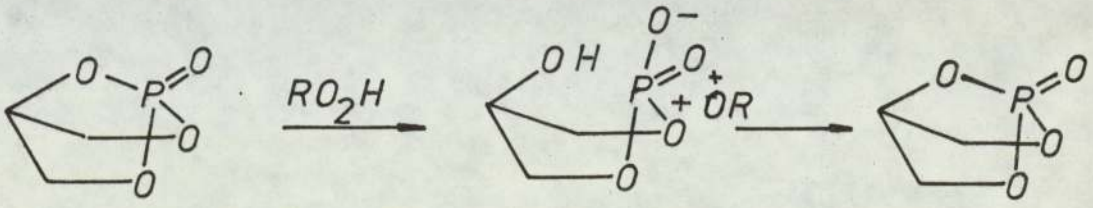
have been shown to exhibit an initial prooxidant effect (29), the corresponding phosphates will be better stabilizers.



Acyclic trialkyl phosphates with suitable electron withdrawing groups may also possess peroxide decomposing ability, and rigid ring systems containing suitable substituents could be synthesized, so the hydroxyl in the ring opened phosphate is fixed and cannot rotate or react with other cyclic units. The system would be assumed to form a pentacoordinate intermediate with hydroperoxide. The following system



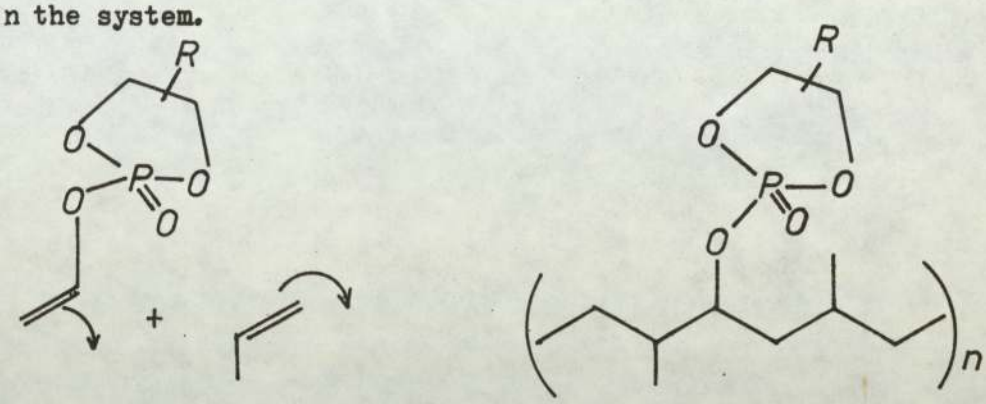
would probably form a six membered ring on reaction with hydroperoxide, and as free rotation of hydroxyl is not possible, the oxanion formed may attack phosphorus, assuming the boat conformation is readily formed,



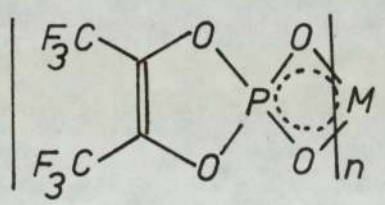
(in cyclohexane-1,4-diol the boat conformation is stable due to hydrogen bonding effects).

The grafting of a phosphate antioxidant into a polymer would be an advantage. The allyl ester of catechol cyclic phosphate could be incorporated into a polymer, and hence the antioxidant would be "fixed" in the system.

e.g.

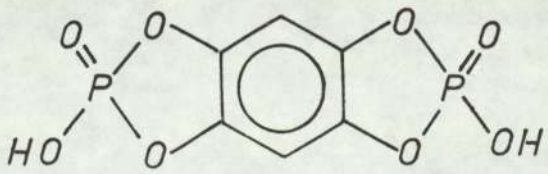


Further work on the oxidation of ketones and olefins is required. The synthesis of naphthalene cyclic phosphate and catechol cyclic phosphate chelates of other transition metals such as Co and Cu would be useful as many Co complexes are known to catalyse oxidation reactions. Metal chelates such as

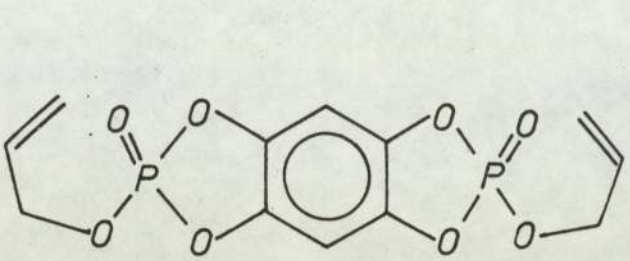


could be evaluated in polymer systems.

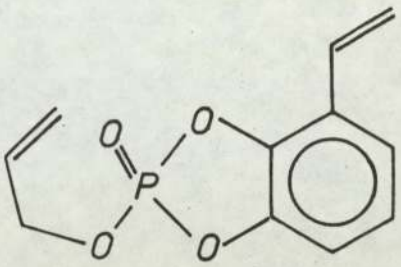
Detailed oxygen absorption studies on all the above compounds would gauge their effectiveness as antioxidants. The preparation of bis cyclo aromatic phosphates and esters thereof for use as anti-oxidants would represent a synthetic challenge e.g.



Polymeric metal chelates could then be obtained. The preparation of allyl esters of the above compound, and those containing vinyl residues would also be of use.

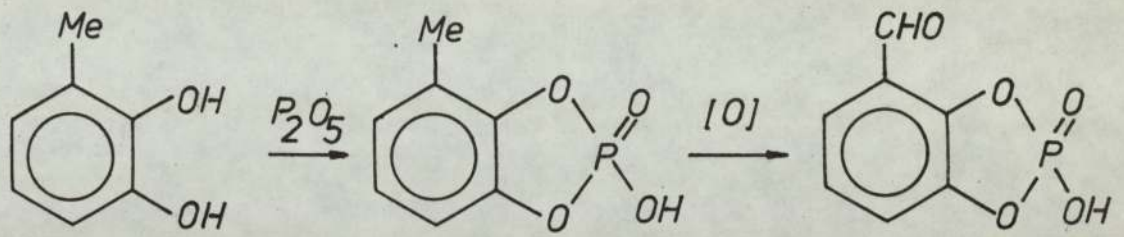


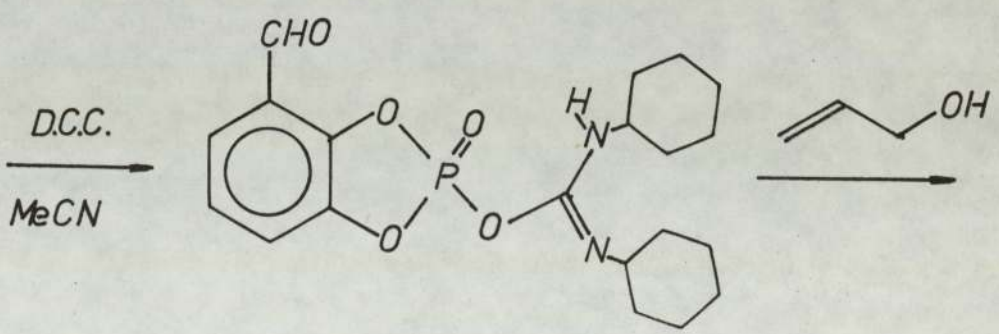
p

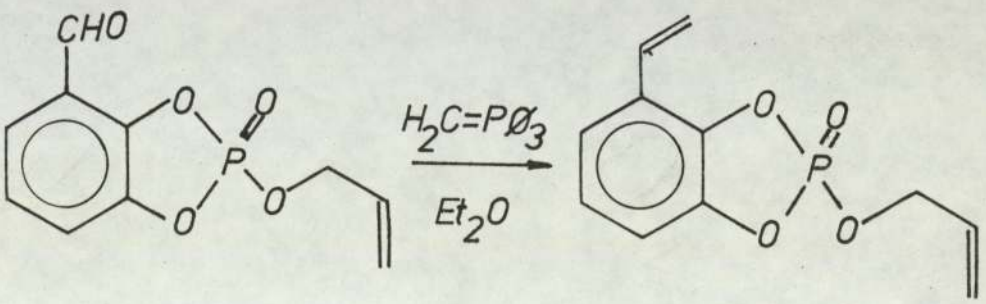


q

As these compounds could be copolymerized with suitable monomers. A suggested route for q is from the corresponding phenol.



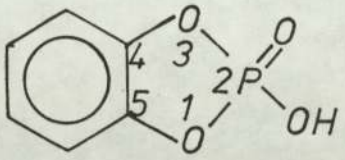




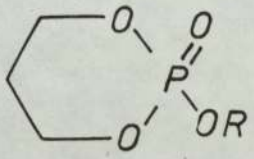
APPENDIX

1. Nomenclature for cyclic phosphate esters.

Throughout the text two conventions have been used for naming the cyclic phosphate esters, either by the ring name, or from the synthetic precursor e.g.



can be called catechol cyclic phosphate, or 2-hydroxy-2-oxo-4,5-benzo-1,3,2-dioxaphospholane. The corresponding six membered ring is designated -1,3,2-dioxaphosphorinane e.g.



is 2-alkoxy-2-oxo-1,3,2-dioxaphosphorinane.

2. Abbreviations used throughout the text.

C.H.P. = Cumene Hydroperoxide

E.B.H.P. = Ethyl benzene Hydroperoxide

D.C.P. = Dicumyl Peroxide

E. = Enzyme

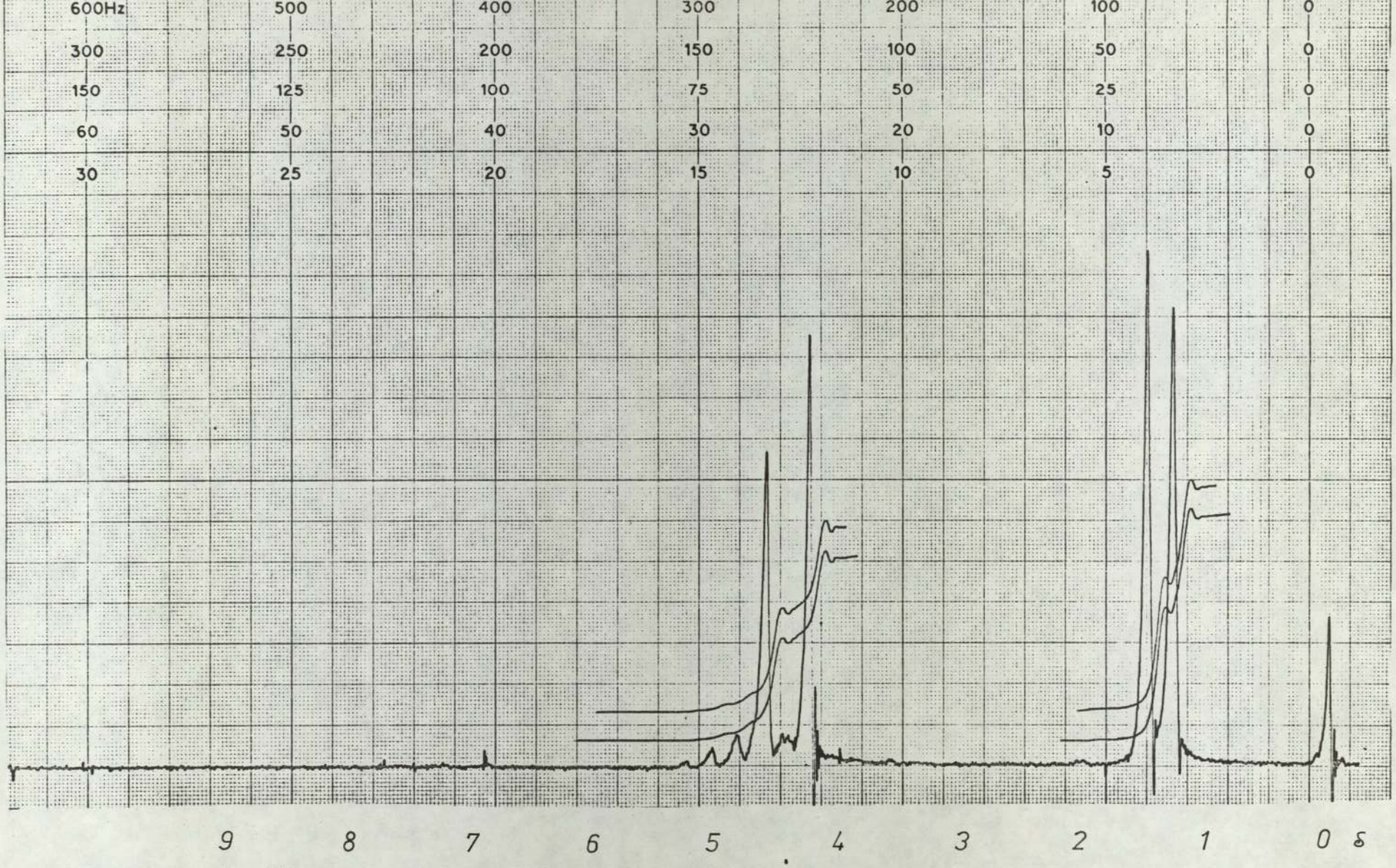
E.C.P. = Ethylene cyclic phosphate

(2-hydroxy-2-oxo-1,3,2-dioxaphospholane)

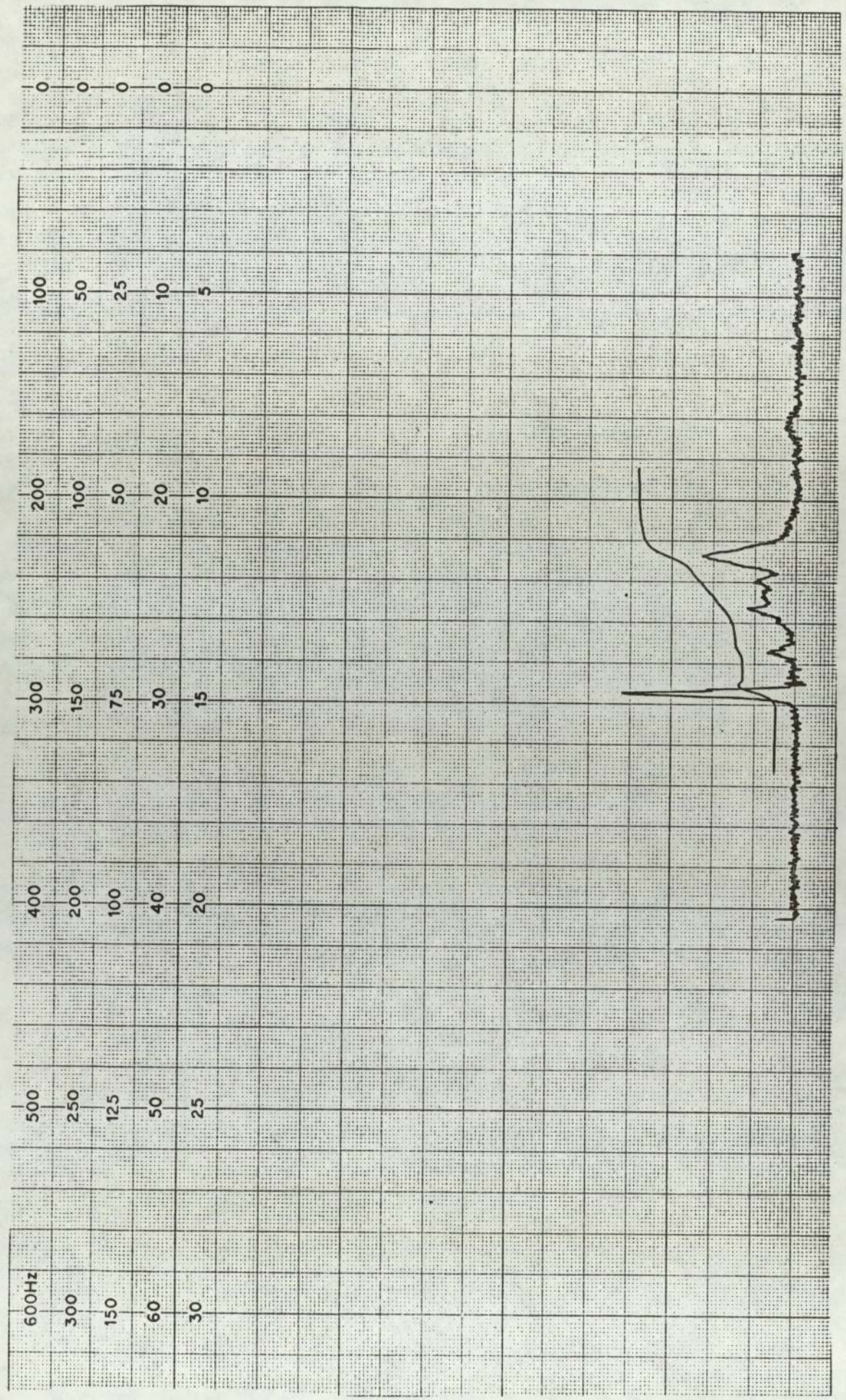
Cyclic esters have been referred to by their preparation number e.g. 2.6.4 = 2-methoxy-2-oxo-4,5-benzo-1,3,2-dioxaphospholane.

3. Selected n.m.r. spectra.

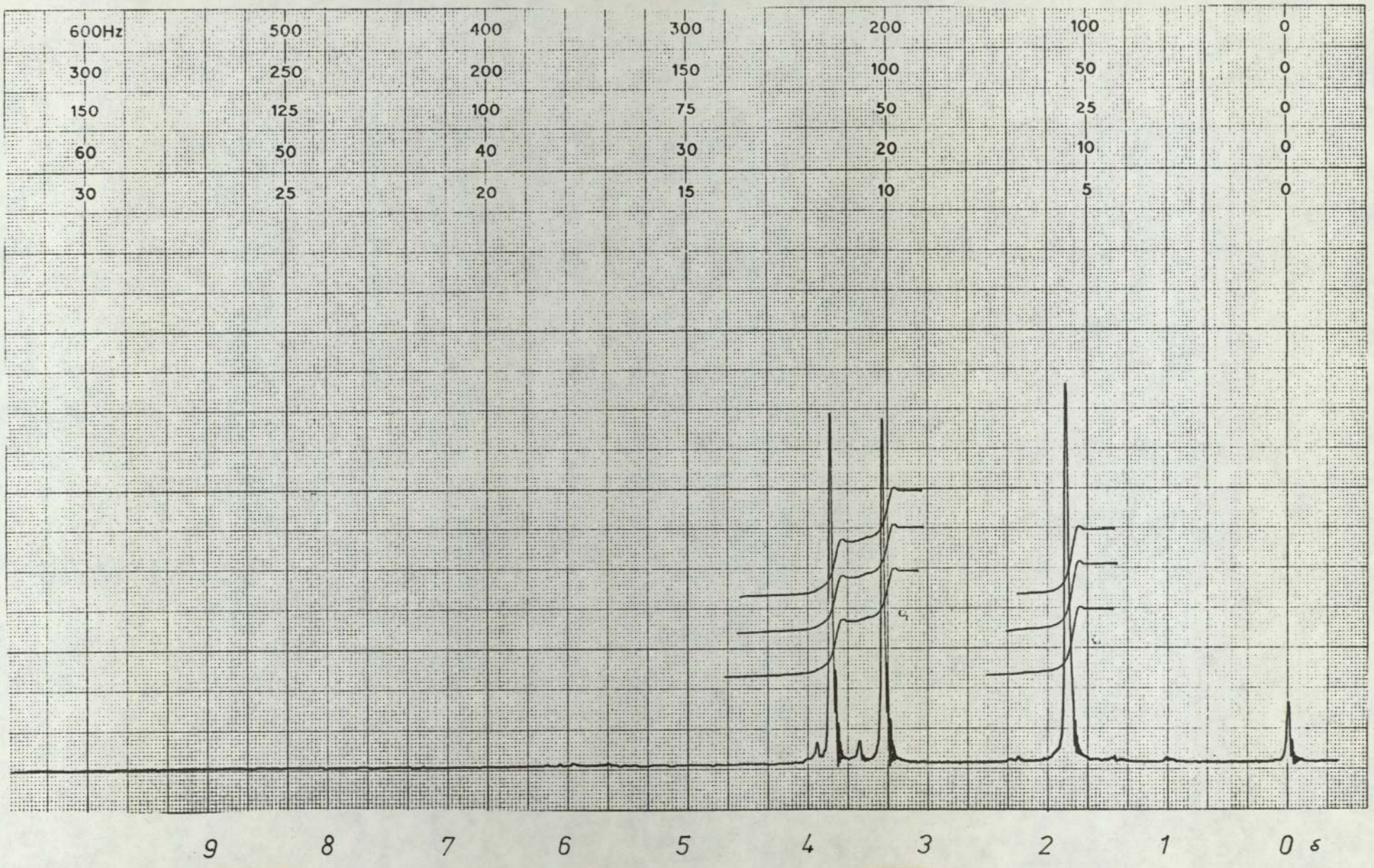
4. The decay curve for the reaction of C.H.P. (0.1 mole) with 2.5.20. (0.01 mole) at 75°C. in chlorobenzene.



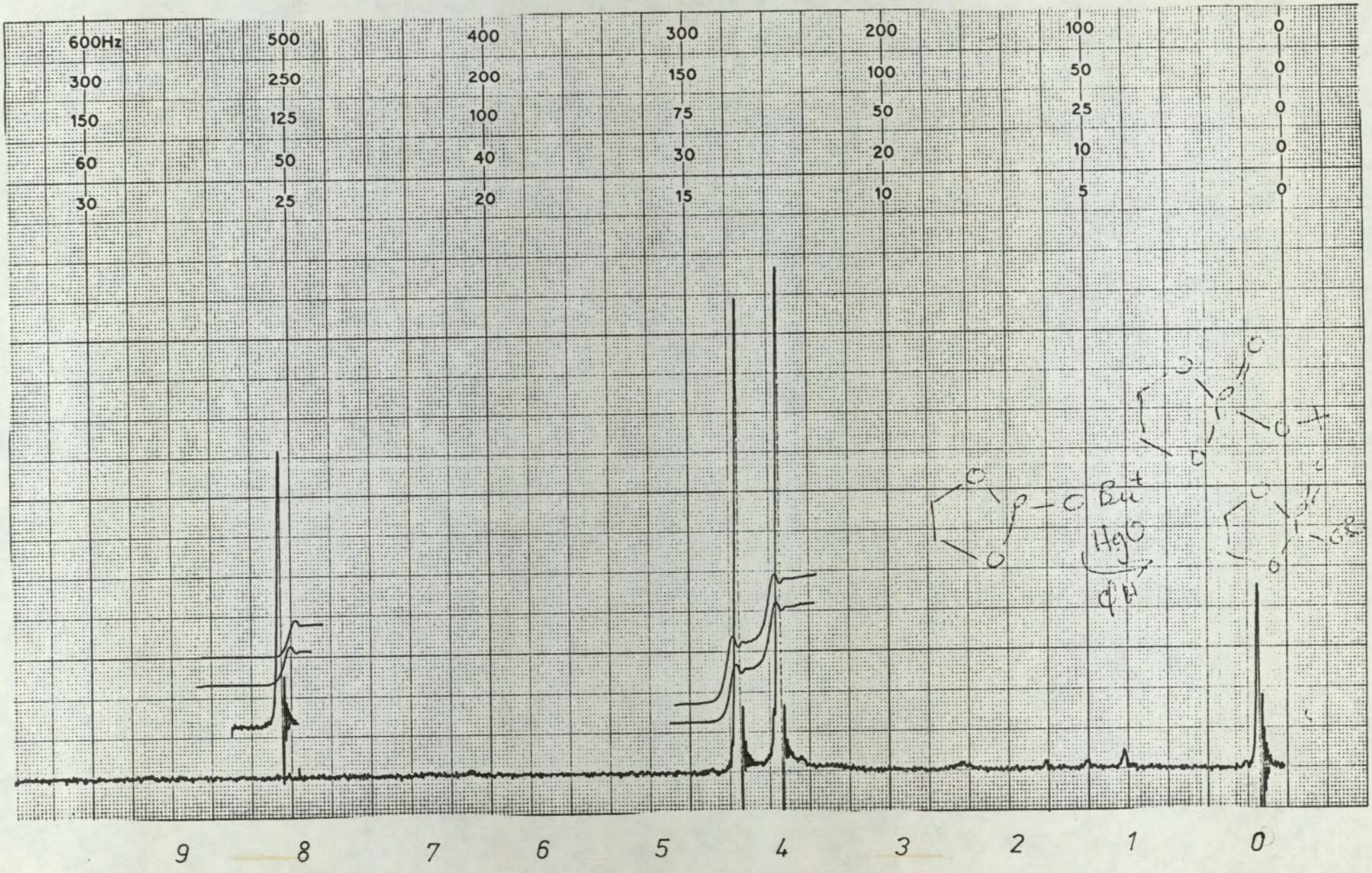
3. The n.m.r. spectrum of 2-oxo-2-isopropoxy-1,3,2-dioxaphospholane in $CDCl_3$.



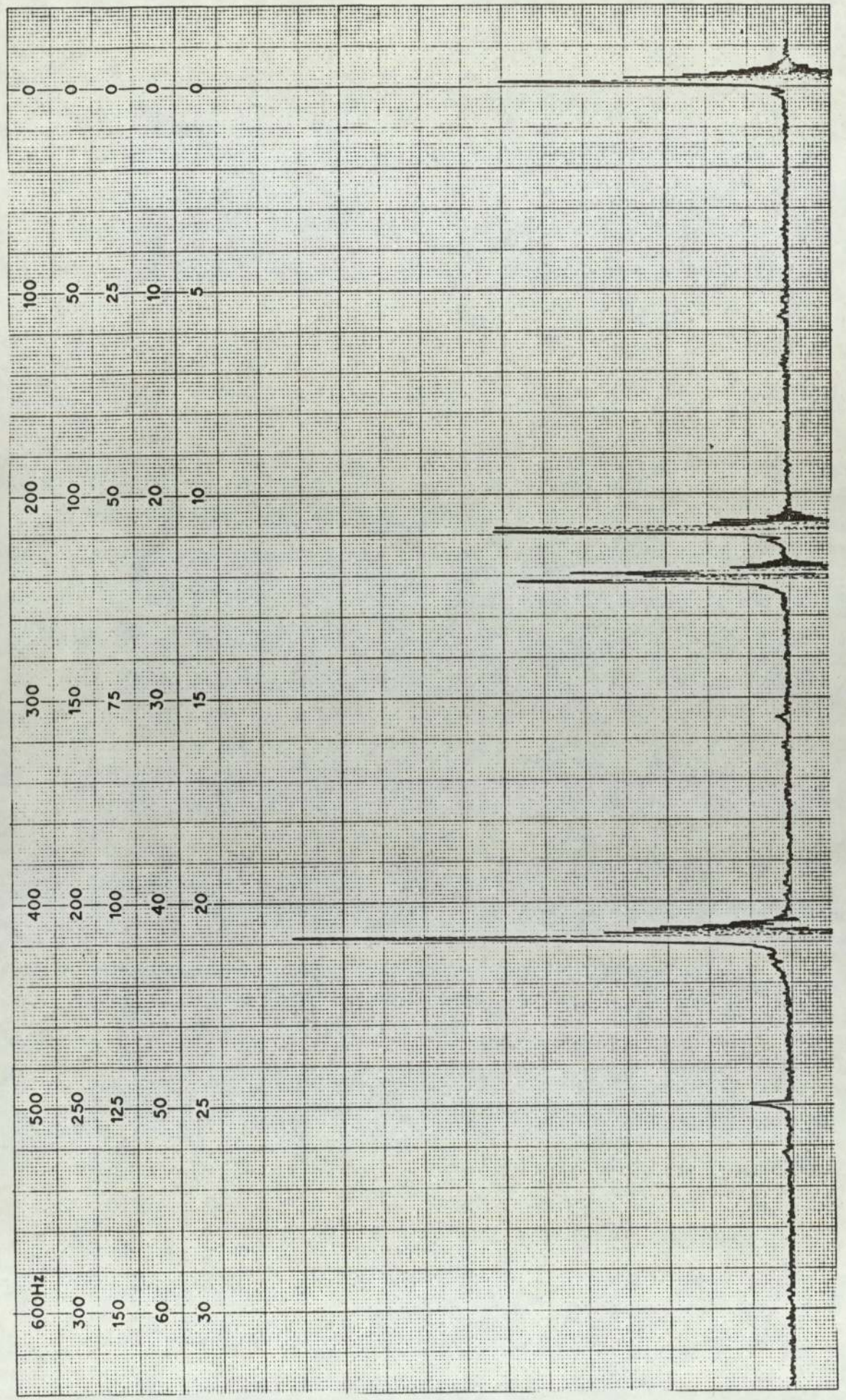
3. The hydrolysis product of E.C.P.



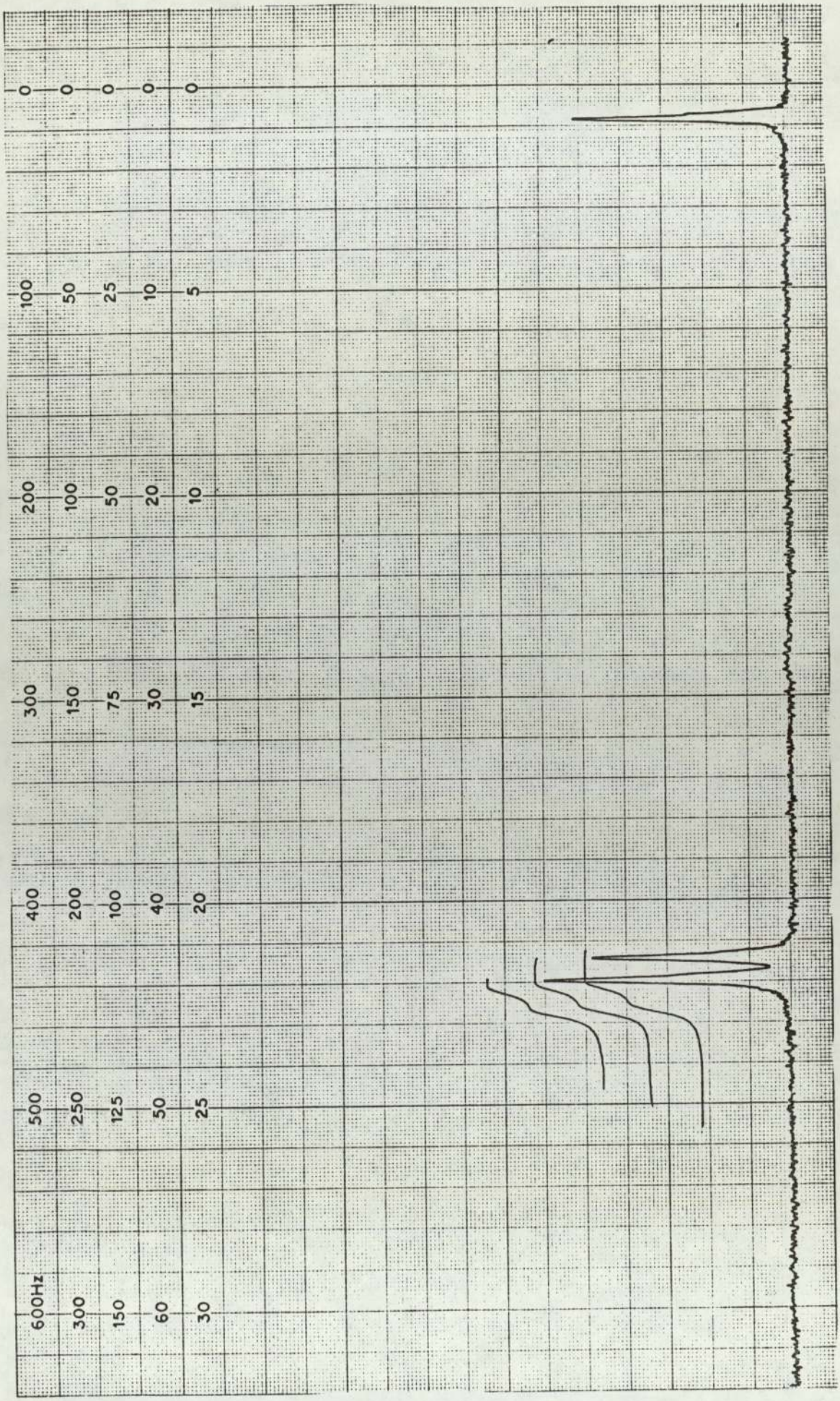
3. The n.m.r. spectrum of 2,2,2-trimethoxy-1,3,2-dioxaphosphol-$\triangle^4$-ene.



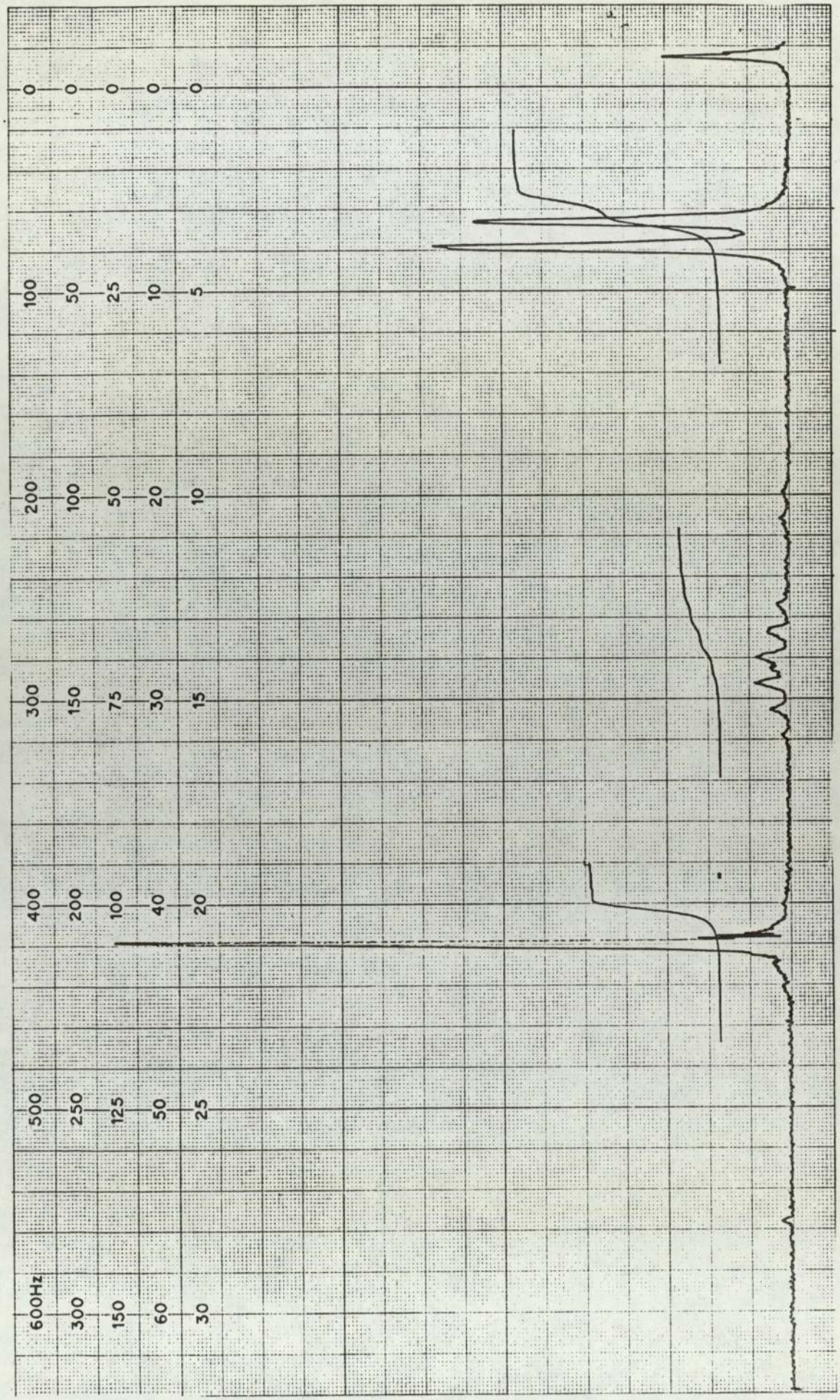
3. The n.m.r. spectrum of 2-hydroxy-2-oxo-1,3,2-dioxaphospholane (E.C.P.) in $DMSO_{d6}$.



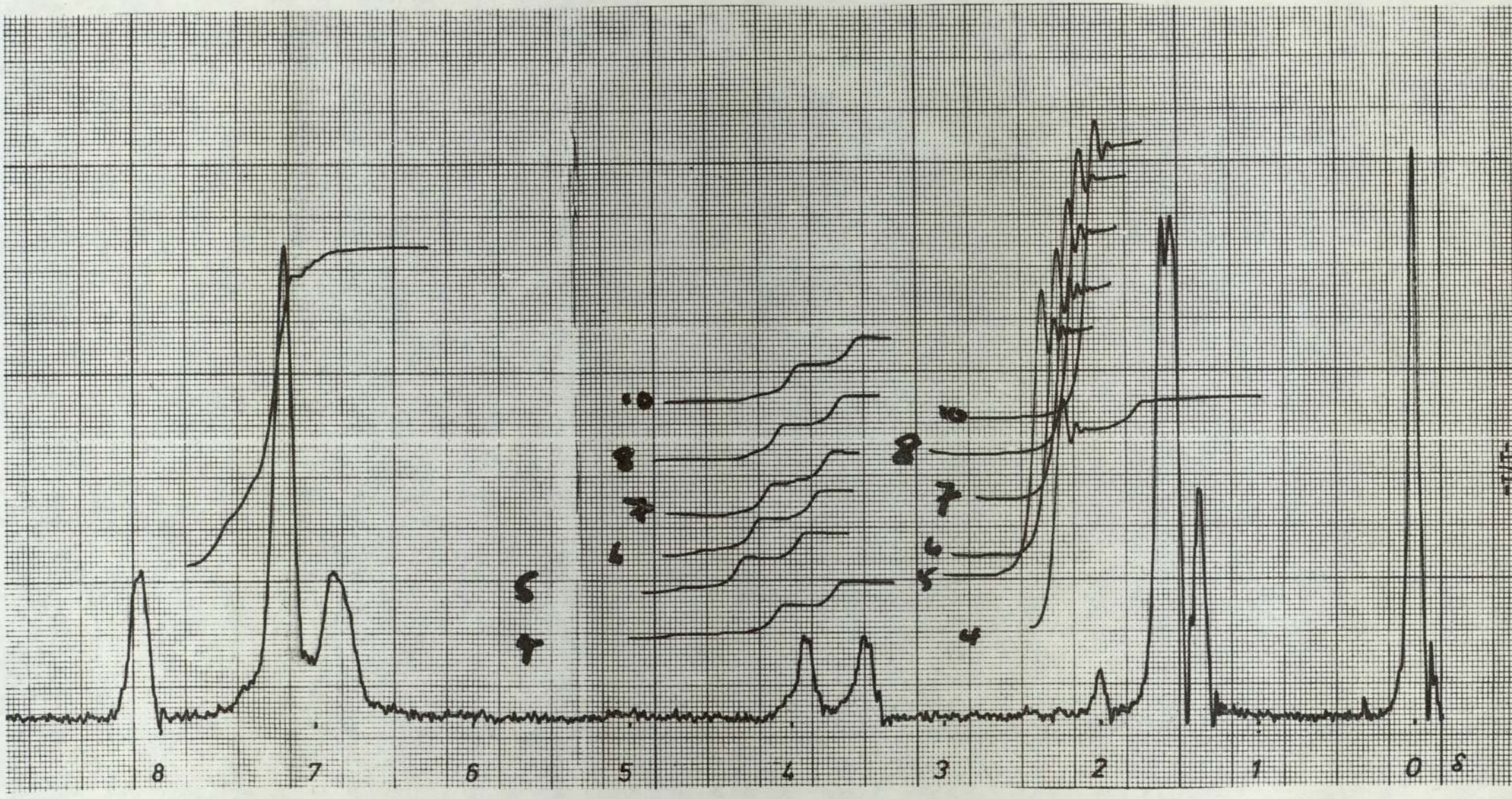
3. The n.m.r. spectrum of 2-methoxy-2-oxo-1,5-benzo-1,3,2-dioxaphospholane in $CDCl_3$.



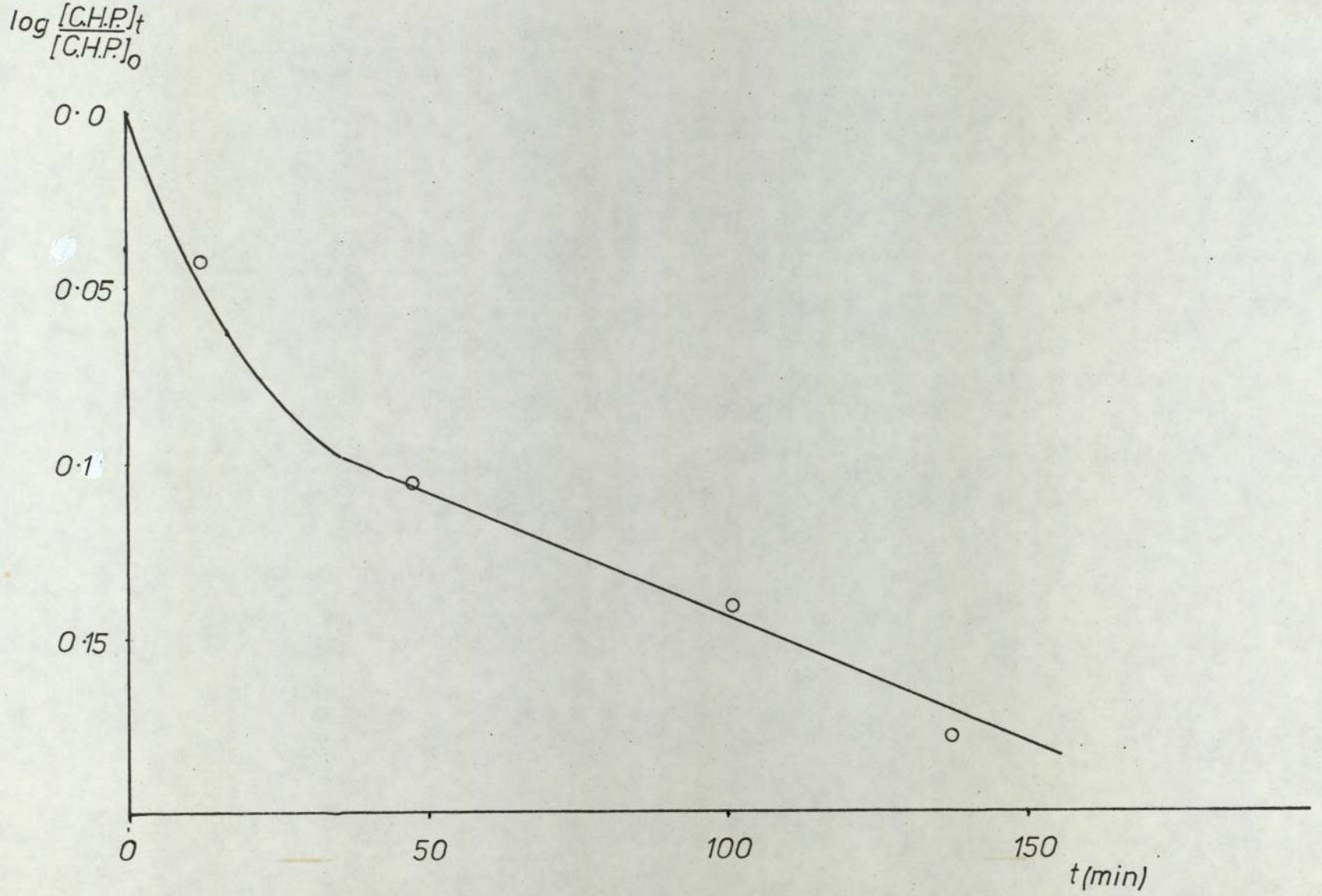
3. The n.m.r. spectrum of 2-oxo-2-phenoxy-4,5-benzo-1,3,2-dioxaphospholane in $CDCl_3$.



3. The n.m.r. spectrum of 2-isopropoxy-2-oxo-4,5-benzo-1,3,2-dioxaphospholane in $CDCl_3$.



3. The n.m.r. spectrum of a mixture of C.H.P. and 2.6.4. in $CDCl_3$ showing a new singlet at τ 8.7.



4. The decay curve for the reaction of C.H.P. (0.1 mole) with 2.5.20. (0.01 mole) at 75 C. in ØCl.

REFERENCES

1 A. Fono , Arkiv Mineral Geol., 24A , No.34 ,(1947)

2 D.M. Brown and A.R. Todd , J. Chem. Soc., 52 , (1952)

3 R. Marksam and J.D. Smith , Biochem J., 52 , 558, (1952)

4 D. Iipkin , P.T. Talbert and M. Cohn , J. Amer. Chem. Soc., 76 , 2871 , (1954)

5 H.A.J. Pieters, "Safety in the Chemical Laboratory", 2nd edition , Butterworth , 1957

6 D.F. Heath , Organophosphorus Poisons , Pergamon , London , 1961

7 R.D. O'Brien , Toxic Phosphorus Esters , Academic Press , New York , 1960

8 J.Voigt , "Die Stabilisierung der Kunstoffe gegen Licht und Warme", Springer Verlag , 1966 , p.316

9 D.G. Pobedimskii , A.L. Buchachenko , Bull. Acad. Sci. U.S.S.R., Division of Chem. Sciences , 1125 , (1968)

10 M.I. Kabachnik , Z. Chem., 2 , 289 , (1961)

11 D.B. Denney , D.Z. Denney , S. Schutzbank , and S.L. Varga Phosphorus , 3 , 99 , (1973)

12 W.G. Bentrude , Tet. Letters , No. 40 , 3543 , (1965)

13 J.B. Plumb and C.E. Griffen , J. Org. Chem., 28 , 2908 , (1963)

14 K.J. Humphris and G. Scott , J. Chem. Soc.,(Perkin II) , 826 , (1973)

15 K.J. Humphris and G. Scott , J. Chem. Soc.,(Perkin II) , 831 , (1973)

16 K.J. Humphris and G. Scott, J. Chem. Soc., (Perkin II), 617, (1974)

17 J. Epstein, M.M. Demek and D.H. Rosenblatt, J. Org. Chem., 21, 796, (1956)

18 J. Epstein and V.E. Bauer, Abstracts of the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Feb. 27, 24, (1956)

19 J.O. Edwards, J. Amer. Chem. Soc., 76, 1540, (1954)

20 J. Epstein, M.M. Demek and D.H. Rosenblatt, J. Amer. Chem. Soc., 78, 341, (1956)

21 T. Wieland and P. Patterman, Angew. Chem., 70, 313, (1958)

22 A.W.D. Avison and J.D. Hawkins, Quart. Revs., 5, 171, (1951)

23 E. Huff and H. Rudney, J. Biol. Chem., 234, 1060, (1959)

24 R.J. Brooks, C.A. Bunton and J.M. Hellyer, J. Org. Chem., 38, 2151, (1973)

25 A.R. Todd et al., J. Chem. Soc., 715, (1961)

26 Eastman Kodak, Fr. 1,365,022 Jun. 26, (1964)

27 C. Ukrami, Y. Goto and H. Kamayana, Bull. Chem. Soc. Japan., 38, (6), 1035, (1965)

28 N. Morikawa et al., Yukagaku, 16, (7), 406, (1967)

29 Ref. 76, p.43

30 H. Myers, Amer. Chem. Soc. Div. Petrol. Chem. Prepr., 13, (2), B61, (1968)

31 A.G. Popev, L.G. Tokareva, N.V. Mikhailov, P.A. Kirpichnikov and L.M. Popeva, Khim. Valokna, 214, (1968)

32 R. Cowling, Ger. Offen. 1,964,567, Jul. 9, (1970)

33 D.G. Pobedimskii, Doklady. Chem., 220, 641, (1975)

34 T. Koizumi et al., Tet. Letters, No. 12, 1075, (1974)

35 M. Daniels, G. Scholes, J. Weiss and C.M. Wheeler, J. Chem. Soc., 226, (1957)

36 G. Scholes, J. Weiss and C.M. Wheeler, Nature, 178, 157, (1956)

37 F. Covitz and F.H. Westheimer, J. Amer. Chem. Soc., 85, 1773, (1963)

38 F.E. Hunter, A. Scott, J. Weinstein and A. Schneider, J. Biol. Chem., 239, (2), 622, (1964)

39 D.Z. Denney, G.Y. Chen and D.B. Denney, J. Amer. Chem. Soc., 91, 6838, (1969)

40 E.T. Kaiser, M. Panar and F.H. Westheimer, J. Amer. Chem. Soc., 85, 602, (1963)

41 G.M. Blackburn, J.S. Cohen and Lord A. Todd, Tet. Letters, No. 39, 2873, (1964)

42 C. Walling and M.S. Pearson, Topics. Phosphorus. Chem., 3, 1, (1966)

43 D.L. Rysavy and S. Slama, Chem. Prumysl., 18, (1), 20, (1968)

44 A. Vogel, A Text Book of Quantitative Inorganic Analysis, 3rd. Edition, Longmans

45 R.M. Johnson and I.W. Siddiqi, Determination of Organic Peroxides, Pergamon, (1970)

46 Ref. 48, p. 280

47 R.D. Mair and A.J. Grauper, Anal.Chem., 36, (1), 194, (1964)

48 A. Vogel , Practical Organic Chemistry

49 The Merck Index , Eighth Edition , 1968

50 M.S. Kharasch , A. Fono and N. Nudenburg , J. Org. Chem., 16 , 113 , (1956)

51 See Ref. 55 p5492

52 T. Yamasaki , T. Sato , Rep. Res. Inst. Tohoku Univ. Ser. A , 6, 384 , (1956)

53 R.S. Edmundson , Chem.and Ind., 1770 , (1962)

54 R.S. Edmundson , Chem. and Ind., 1828 , (1962)

55 H.J. Lucas , F.W. Mitchell , J.R. and C.N. Scully , J. Amer. Chem. Soc., 50 , 5491 , (1950)

56 R.S. Edmundson , Chem. and Ind., 1828 , (1962)

57 J.R. Cox , R.E. Wall and F.H. Westheimer , Chem. and Ind., 929 , (1959)

58 R. Wilcox , G. Harris and R. Olson , Tet. Letters , No.57 , 6001 , (1968)

59 R.S. Edmundson and A.J. Lambie , J. Chem. Soc., B , 577 , (1967)

60 J.R. Cox and M.G. Newton , J. Org. Chem., 34 , 2600 , (1969)

61a F. Ramirez et al , J.Amer.Chem.Soc. , 85 , 3252 , (1963)

61 P.C. Crofts , J.H.H. Markes , and H.N. Rydon , J. Chem. Soc., 4250 , (1958)

62 L. Anschutz , Annalen , 454 , 112 , (1927)

63 T.A. Khawaja and C.B. Reese , J. Amer. Chem. Soc., 88 , 3446 , (1966)

64 T.Koizumi et al., Tet. Letters , No.12 , 1075 , (1974)

65 E. Cherbuliz , M. Schwarz and J.P. Leber , Helv. Chim. Acta. , 34 , 841 , (1951)

66 M. Eto and Y. Oshima , Agr. Biol. Chem. (Tokyo) , 26 , 452 , (1962)

67 J.R. Cox , R.E. Wall and F.H. Westheimer , Chem. and Ind., 929 , (1959)

68 L. Keay and E.M. Crook , J. Chem. Soc., 710 , (1961)

69 F. Ramirez and O.P. Madan, J.Amer.Chem.Soc., 87 , 670, (1965)

70 E. Gaydon , R. Freeze and G. Buono , Bull. Soc. Chim. (Fr.), No.7 , 2281 , (1973)

71 A. Coomerasamy , Ph.D. Thesis , Aston , 1973

72 F.H. Seubold and W. Vaughan , J. Amer. Chem. Soc., 75 , 3790 , (1953)

73 U.S. Patent , 2994719 , Aug.1 1961

74 L.F. Fieser and M. Fieser, Advanced Organic Chemistry, p. 377, Reinhold (1963)

75 F.H. Westheimer , Accounts Chem. Res., 1 , 70 , (1968)

76 K. Humphris , Ph.D. Thesis , Aston , 1971

77 G. Scott , Private Communication

78 J. Chem. Soc., (Perkin II) , 1101 , (1974)

79 R.S. Berry , J. Chem. Phys., 32 , 933 , (1960)

80 R.F. Hudson , Accounts Chem. Res., 5 , 204 , (1972)

81 The use of the singlet oxygen apparatus of A. Scott of this University is gratefully acknowledged

82 K. Laidler, Reaction Kinetics, McGraw Hill, (1965), p. 244

83 See Ref. 50 , p123.

84 F.H. Seubold and W. Vaughan , J. Amer. Chem. Soc., 75 , 3790 , (1953)

85 K. Laidler, Chemical Kinetics, p. 242, McGraw Hill (1965)

86 C. Hertzer, Publ. Sci. Tech. Min. Air Fr., No. 153, 94, (1966)

87 D. Rysavy and S. Slama, Chem. Prumysl., 18, (1), 20, (1968)

88 F.H. Westheimer, Chem. Soc. Spec. Publ., 8, 1, (1957)

89 V V. Rode and T.N. Balykova, Doklady Chem., 176, 85, (1967)

90 Ref. 41, p. 2875

91 M.L. Tomayo, Chem. Abs., 45, 7046e, (1951)

92 E.T. Kaiser and K. Kudo, J. Amer.Chem. Soc., 89, 6725, (1967)

93 R.S. Edmundson and A.J. Lambie, J. Chem. Soc., 577, (1967)

94 Ref. 71, p. 134

95 R.A. Sheldon and J.A. Van Doorn, J. Catal., 34, 242, (1974)

96 F. Jardon, M.Sc. Thesis, Aston, (1975)

97 M.N. Sheng and J.G. Zajacek, J. Catal., 418, (1967)

98 E.T. Kaiser, W.T.S. Lee and F.P. Boer, J. Amer. Chem. Soc., 93, 2351, (1971)

99 H. Gross and D. Buchardson, J. Amer. Chem. Soc., 92, 4699, (1970)

100 J.H. Hudena and E.T. Kaiser, J. Amer. Chem. Soc., 89, 460 (1967)

101 F.H. Westheimer et al., J. Amer. Chem. Soc., 91, 6066, (1969)

102 A. Baeyer and V. Villiger, Ber., 32, 3625, (1899)

103 A. Baeyer and V. Villiger, Ber., 33, 858, (1900)

104 S.L. Friess and R. Pinson, J. Amer. Chem. Soc., 74, 1302, (1952)

105 J.C. Robertson and A. Swelim, Tet. Letters, (30), 2871, (1967)

106 J.D. McClure and P.H. Williams, J. Org. Chem., 27, 24, (1962)

107 L.F. Fieser and M. Fieser, Advanced Organic Chemistry, p. 428 Reinhold, New York, (1967)

108 W.L. Hawkins, Polymer Stabilization, Wiley-Interscience, New York, p. 180, (1972)

109 D.J. Carlsson and D.M. Wiles, Macromolecules, 2, 597, (1969)

110 K. Tsuji et al., Polymer J., 1, 133, (1970)

111 D.J. Carlsson and D.M. Wiles, Macromolecules, 2, 587, (1969)

112 A.M. Trozzolo and F.H. Winslow, Macromolecules, 1, 98, (1968)

113 K. Tsuji and T. Seiki, J. Polymer Sci., B, 10, 139, (1972)

114 D.J. Harper and J.F. McKellar, Chem. and Ind., 848, (1972)

115 D.C. Mellor, A.B. Moir and G. Scott, Europ. Polym. J., 9, 219, (1973)

116 K.J. Humphris and G. Scott, Ger. Offen., 2,342,928, Mar. 7, (1974)

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