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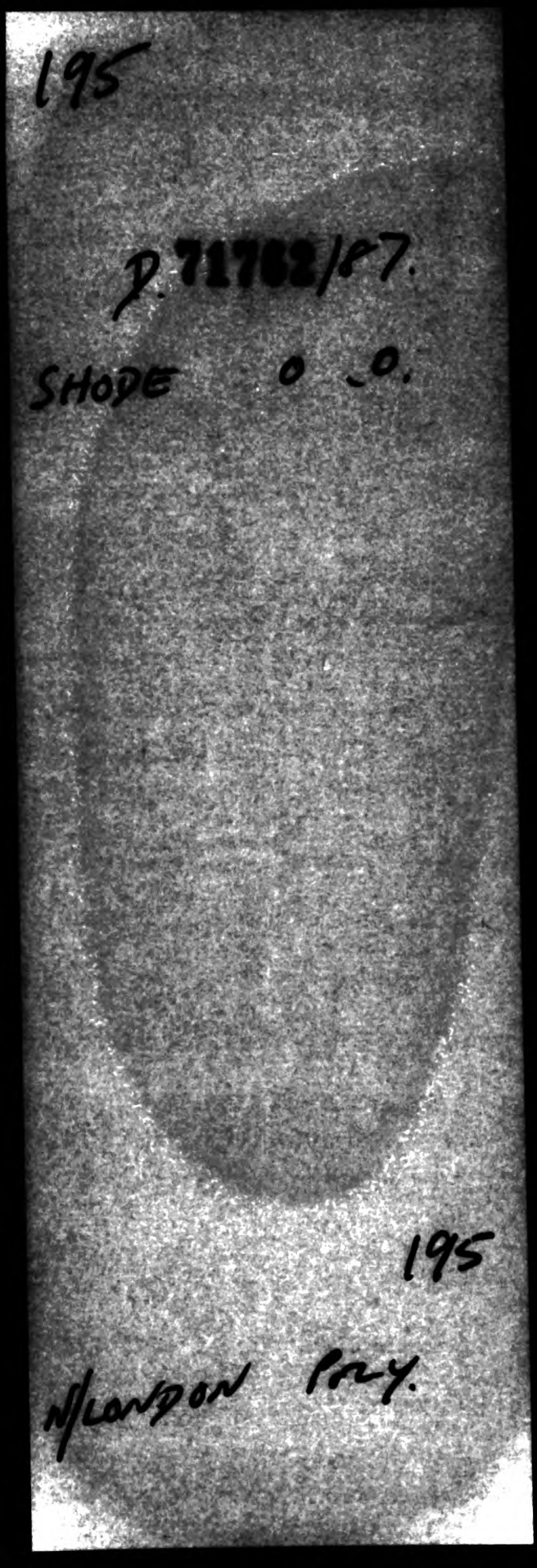
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A Thesis entitled

THE REACTIONS OF ESTERS OF PHOSPHORUS(III) ACIDS WITH ELECTROPHILIC REAGENTS

Submitted to the Council for National Academic Awards in partial fulfilment of the requirements for the degree of

Doctor of Philosophy

by

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ABSTRACT

REACTIONS OF ESTERS OF PHOSPHORUS(III) ACIDS WITH ELECTROPHILIC REAGENTS.

BY OLUYEMISI OLABISI SOWUNMI (MRS)

Reactions of highly hindered phosphorus(III) esters derived from 2,2,2-triphenylethanol, 2,2-diethylbutan-1-ol, and norbornan-1-ol with electrophilic reagents, in particular α-haloketones, were studied by ^{31}P and ^{1}H n.m.r. spectroscopy.

The phosphite ester derived from 2,2,2-triphenylethanol could not be obtained, as it readily undergoes elimination, although the diphenylphosphinite was prepared and gave a stable Arbuzov intermediate on reaction with iodomethane.

Tris(2,2-diethylbutyl) phosphite reacted in a similar manner to previously obtained trineopentyl phosphite. The increased bulk of the β-substitutents in the 2,2-diethylbutyl group, compared to those in neopentyl, does not appear to increase the resistance to S$_N$2 attack to any significant extent.

Trinorborn-1-yl phosphite reacted with a variety of α-haloketones to give quasiphosphonium halides of unusually high stability, including the first example of a stable Perkow intermediate, to be obtained from a trialkyl phosphite. Unusual features of the reactivity of the phosphite were its complete lack of reaction at room temperature with either chloroacetone or phenacyl chloride, (which give vinyl phosphates readily with trialkyl phosphites in general), and the unexpected formation of both the vinyloxy- and keto-phosphonium chloride with chloroacetone and phenacyl chloride at 69 °C. A vinyloxyphosphonium (Perkow) intermediate is isolated, however, from α-chloro-p-nitroacetophenone at room temperature and is the first example of a stable compound of this type.

The tri-(norborn-1-yloxy)phosphonium salts showed high thermal stability, the methiodide being resistant to decomposition at 150 °C. The ketophosphonium salts yielded the expected Arbuzov products, whereas the Perkow intermediate underwent preferential cleavage of the vinyloxy groups to yield trinorborn-1-yl phosphate.

^{31}P n.m.r. chemical shifts for the trinorborn-1-yloxyphosphonium salts, for their Arbuzov cleavage products when formed, and also for trinorborn-1-yl phosphate are significantly upfield from those of simpler acyclic analogues although the signal for trinorbornyl phosphite itself is in the expected region.

Fast atom bombardment mass spectrometry was found to be useful in characterising the quasiphosphonium halides isolated by the appearance of the phosphonium ion in the positive ion spectrum, sometimes as the base peak. X-ray structural determinations on the Arbuzov, and the Perkow intermediates isolated, showed the phosphonium salts to be distorted tetrahedral phosphonium ions with minimum P....X distances of 4.58 and 4.71 Å respectively, and also a significant double bond character in the bonds between the positively charged phosphorus and the oxygen atoms.

The effect of silver perchlorate in the reaction of trimethyl phosphite and iodoacetone was investigated, and found to give trimethyl phosphate and tetramethyl pyrophosphate, with no Arbuzov intermediate or product detected as previously claimed.

ACKNOWLEDGEMENTS

I would like to express my gratitude to my supervisors, Dr. H.R. Hudson and Dr. R.W.Matthews, for their suggestion of the topic, guidance and constant encouragement throughout the course of this research.

I would also like to express my gratitude to my external collaborators, Professor L. Tőke and Dr. I. Petneházy for many helpful discussions and suggestions.

Thanks are also due to: Dr. E.M. McPartlin for assisting with the X-ray crystallographic analysis and for much valuable advice on crystal structure; Mr J. Crowder for carrying out the n.m.r. spectroscopy and for his valuable assistance in the interpretation; Dr. C.S. Creaser of East Anglia University for carrying out the fast atom bombardment mass spectrometry of some of the compounds, for helpful discussions on the technique and the interpretation of the spectra; Mr. C.J. Cooksey of University College London, for ^{1}H n.m.r. (200 MHz) spectroscopy; and to all members of the School of Chemistry who have helped to make this work possible.

Finally, I would like to thank the Polytechnic of North London for a Research Assistantship.

This thesis is dedicated to my parents, Surajudeen and Modupe Obisesan, my husband, Olufemi, and to all other members of my husband's family and mine, without whom I could not have done this work.

CONTENTS

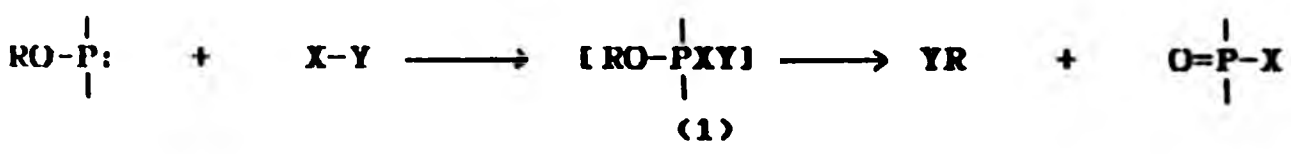
Chapter 1

HISTORICAL

1 **Historical**

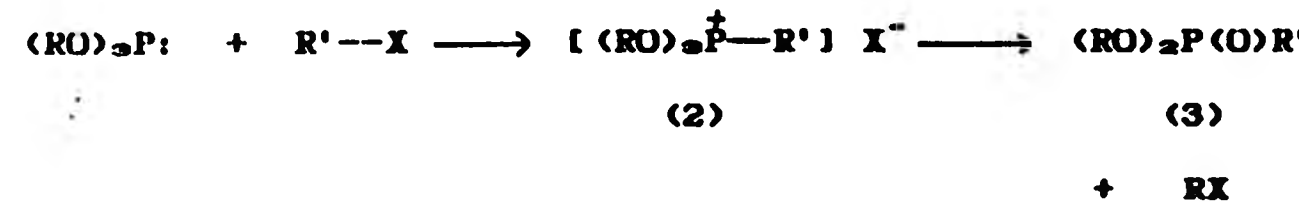
The research aim was to investigate the mechanisms by which phosphorus(III) esters interact with electrophilic reagents, in particular α-haloketones and to study the intermediates which are involved.

In reactions with electrophiles such as RX, HX, X_2 (X = halogen) a quasiphosphonium intermediate (1) may be detected or even isolated if a sterically hindered alkyloxy group is present[1-3] and in special cases a 5-coordinate intermediate may be formed.[4] Trialkyl phosphite with alkyl



(1)

halide undergoes the Michaelis-Arbuzov reaction to yield dialkyl alkylphosphonate (3). The mechanism of the reaction leading to the formation of the new carbon-phosphorus bond involves a nucleophilic attack by the phosphorus atom on the α-carbon of the alkyl halide to give an intermediary quasiphosphonium salt (2) which is stabilized by the loss of alkyl halide and formation of the phosphonate (3) by an S_N2 reaction.



(2) (3)

Aromatic and aliphatic acid chlorides also undergo the Michaelis-Arbuzov reaction with trialkyl phosphite to yield the corresponding phosphonate (5) *via* the quasiphosphonium intermediate (4).[8]

$$(RO)_3P + ArCOCl \longrightarrow [(RO)_3\overset{+}{P}COAr]\ Cl^-$$

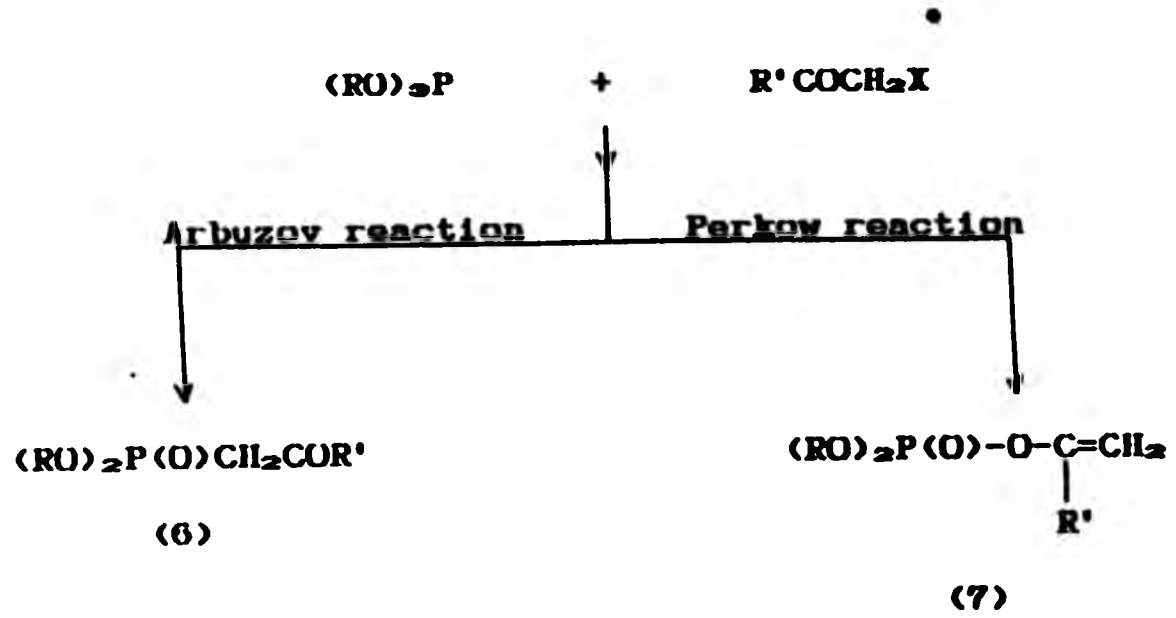
(4)

$$\downarrow$$

$$(RO)_2P(O)COAr + RCl$$

(5)

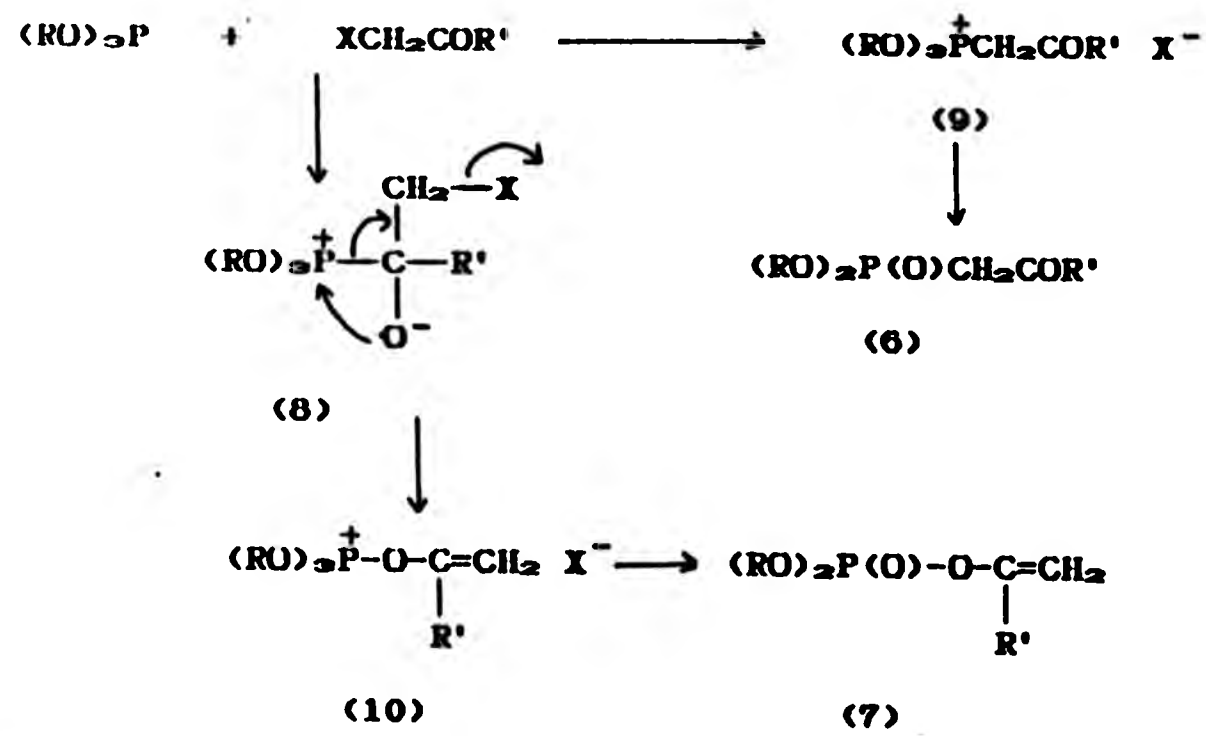
Reactions of α-halogenoketones with trialkyl phosphites are of particular interest as they undergo either the Arbuzov reaction, which yields the ketophosphonate (6) or they may undergo the Perkow reaction, which yields the vinyl phosphate (7) or a mixture of both reactions.[4-6]



(Scheme 1)

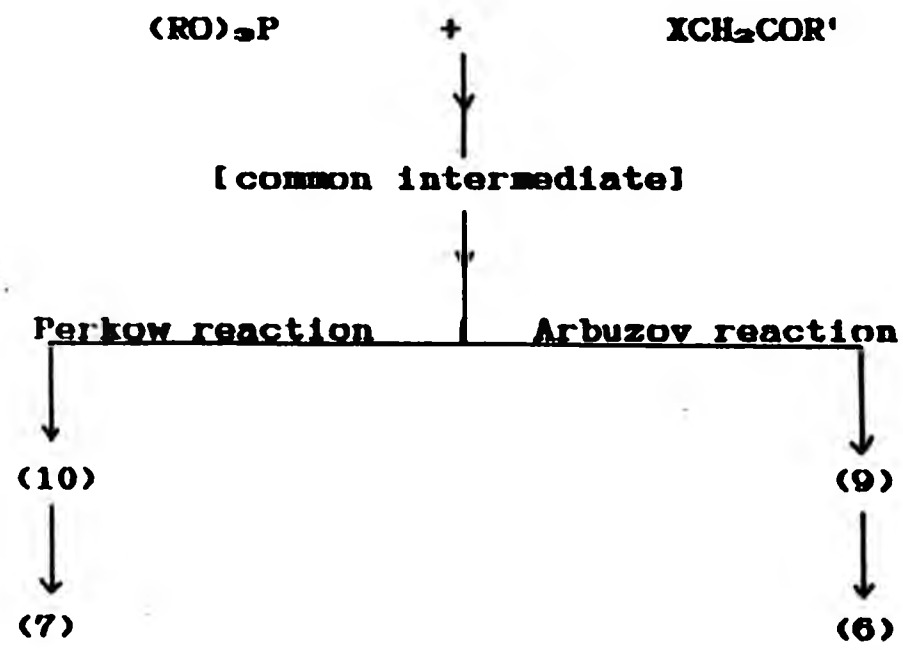
Several factors,[8] including solvent, temperature and the nature of the halogen influence the product ratio of ketophosphonate to vinyl phosphate. Low temperature and a more electronegative halogen favour the vinyl phosphate. Substituents on the α-carbon, especially electron-withdrawing groups, also favour the Perkow reaction. Reactions of this type have achieved commercial importance as a route to the insecticidal enol phosphate esters[9] and other industrially useful products.

The Arbuzov product was first thought to have resulted from the initial attack by phosphorus at the α-carbon atom, while the Perkow product was formed by initial attack at the carbonyl carbon atom followed by migration of phosphorus from carbon to oxygen (Scheme 2).[10] However, certain



(Scheme 2)

kinetic studies, have indicated that a common first intermediate may be involved in both reaction pathways



(Scheme 3)

(Scheme 3).[11,12] A considerable amount of research interest has been generated in the Arbuzov and Perkow reaction mechanisms but although they have been extensively investigated by various workers,[12-16] the reactions are not yet fully understood. The difficulty lies in the fact that there are four possible sites for nucleophilic attack at an α-halocarbonyl compound (Scheme 4).[10]

Attack at the α-carbon [Scheme 4(i)], followed by formation of vinyl phosphate (7) from the ketophosphonium intermediate (9) *via* a four-membered cyclic phosphorane (11) was excluded by Hudson *et al.*[12], who isolated the first ketophosphonium and vinyloxyphosphonium halides by the use

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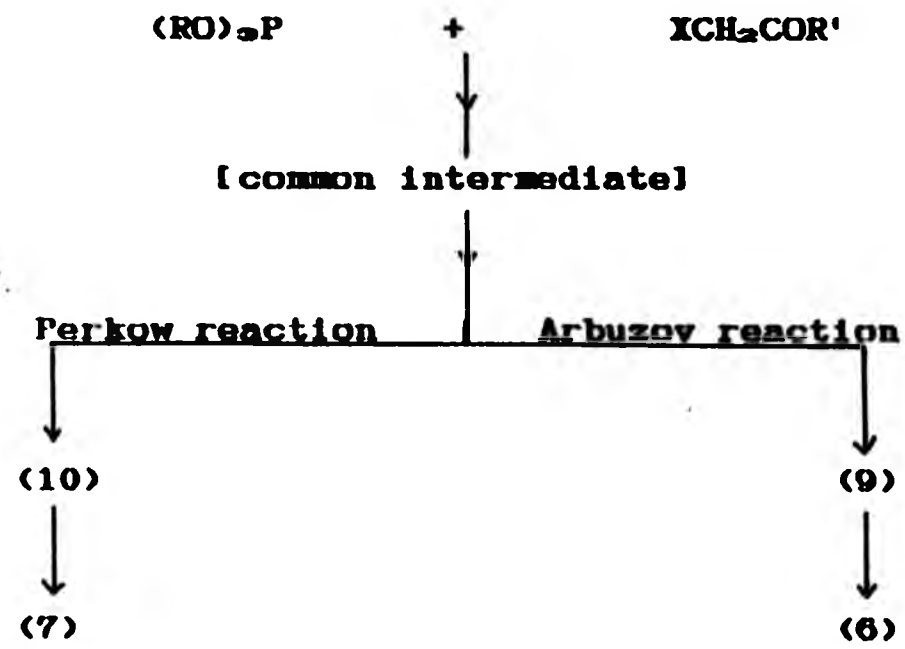

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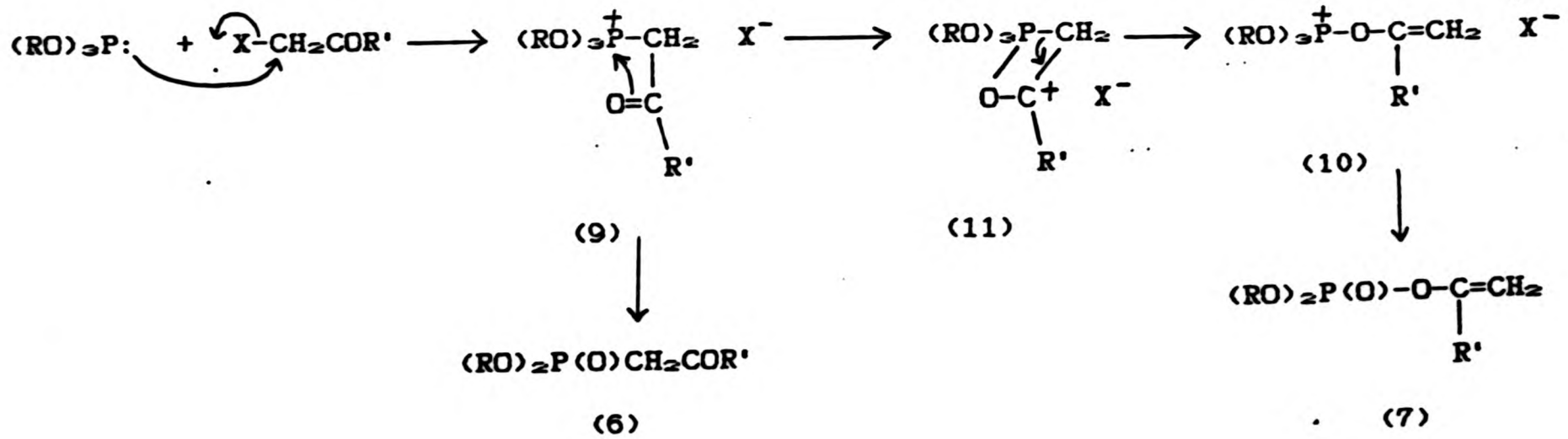
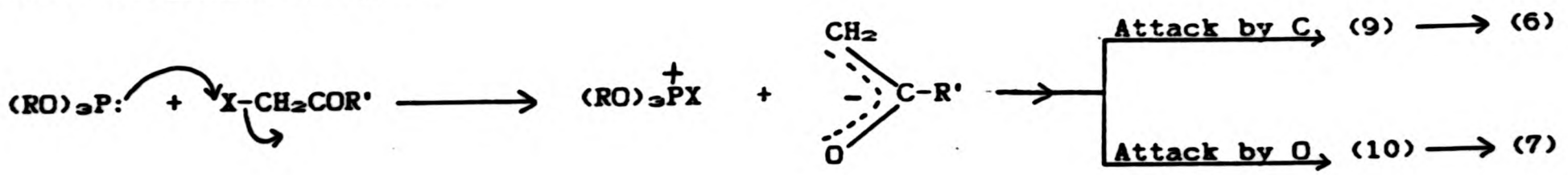
(i) Attack at the α-carbon:

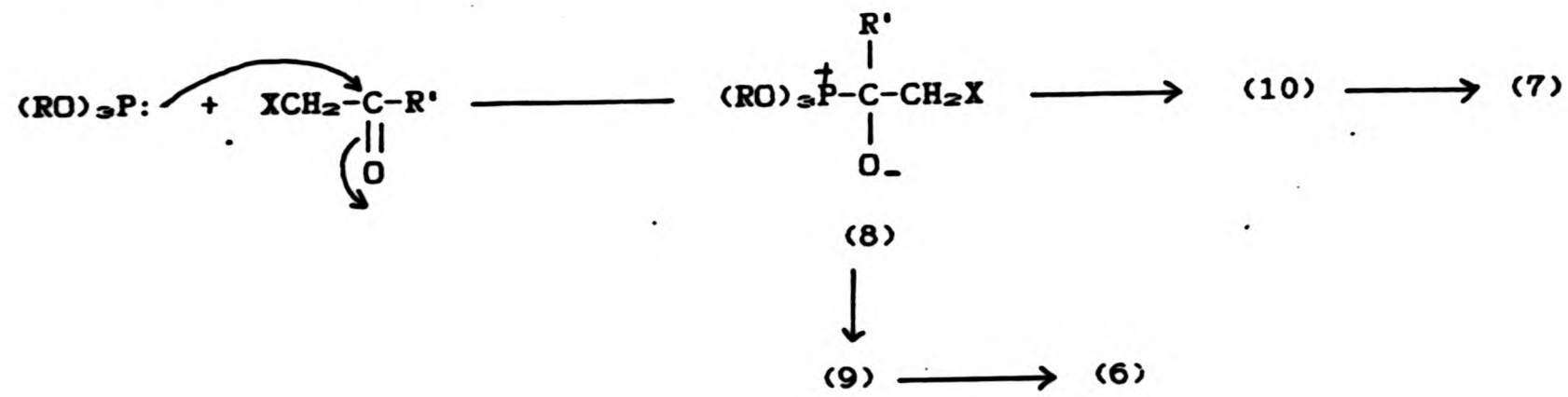


(ii) Attack on halogen:

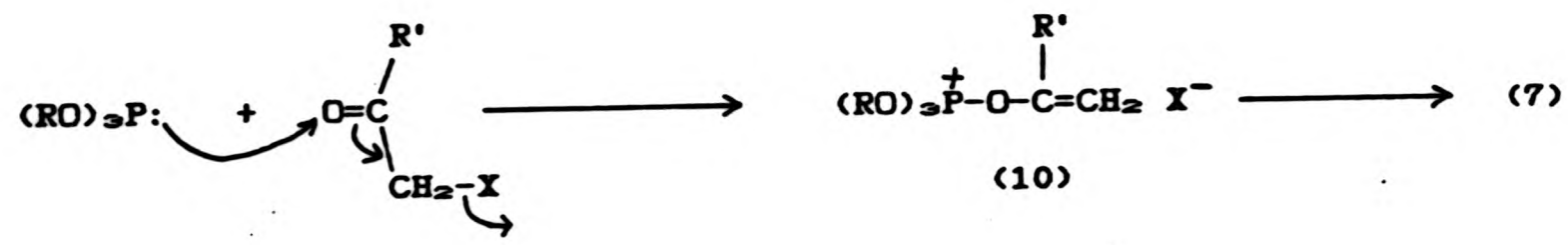


(Scheme 4)

(iii) Attack on carbonyl carbon:

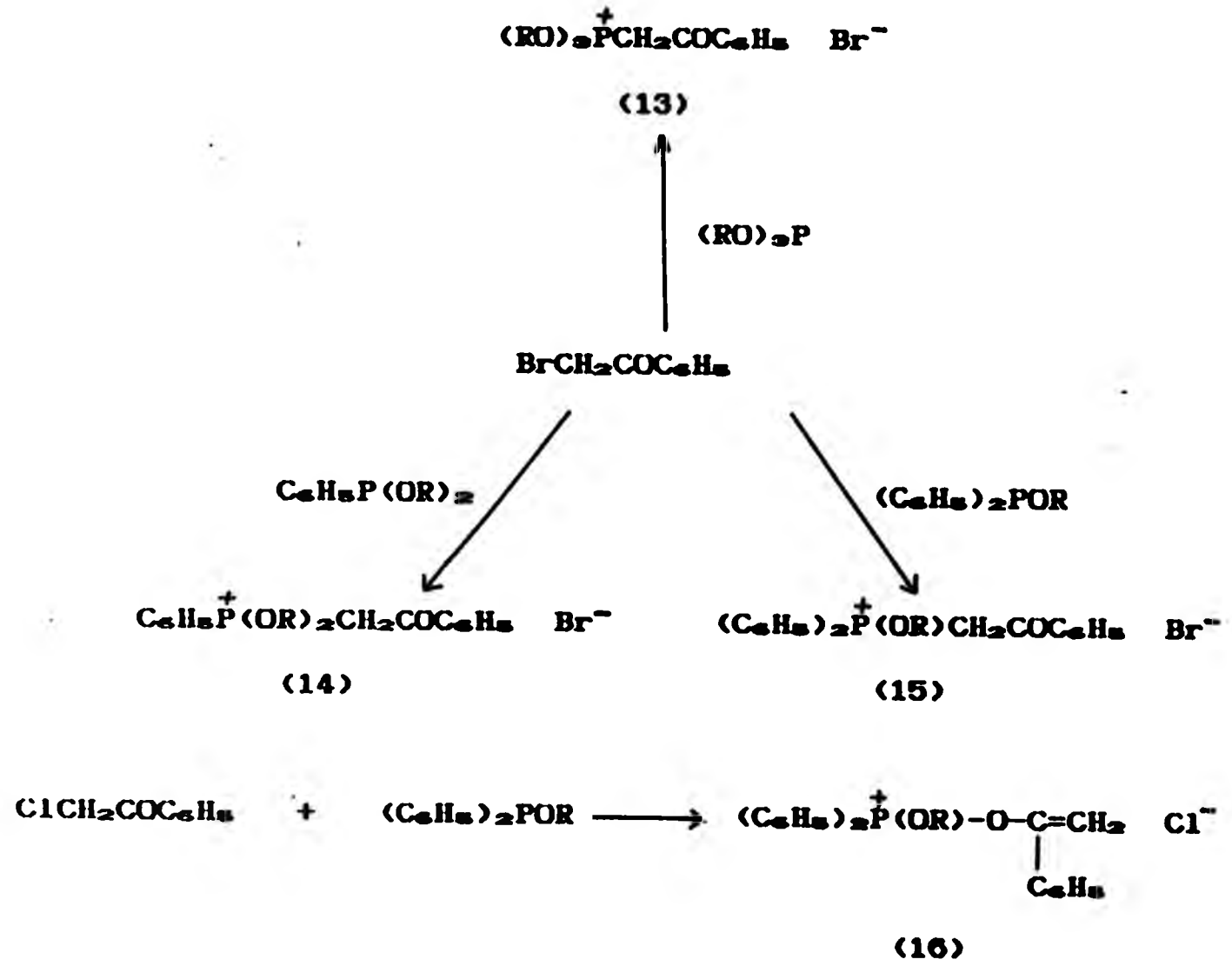


(iv) Attack on carbonyl oxygen:



(Scheme 4 continued)

of sterically hindered neopentyl esters (Scheme 5). The steric resistance of the neopentyl group to S_N2 attack



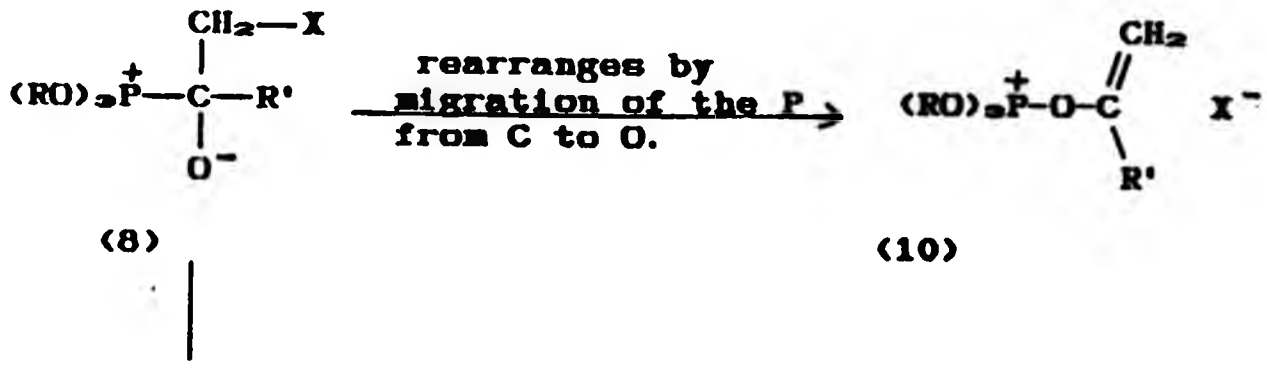
(Scheme 5)

favours the build up of sufficient concentration of the intermediates to be isolated. Decomposition of the phosphonium salts gave only the corresponding Arbuzov or Perkow products, even in acetone-acetic acid mixture in

which trineopentyl phosphite and α-bromoacetophenone were shown to give dineopentyl 1-phenylvinyl phosphate (Perkow product) as the major product. Trineopentyloxy(phenacyl)-phosphonium bromide (13) gave only the ketophosphonate.

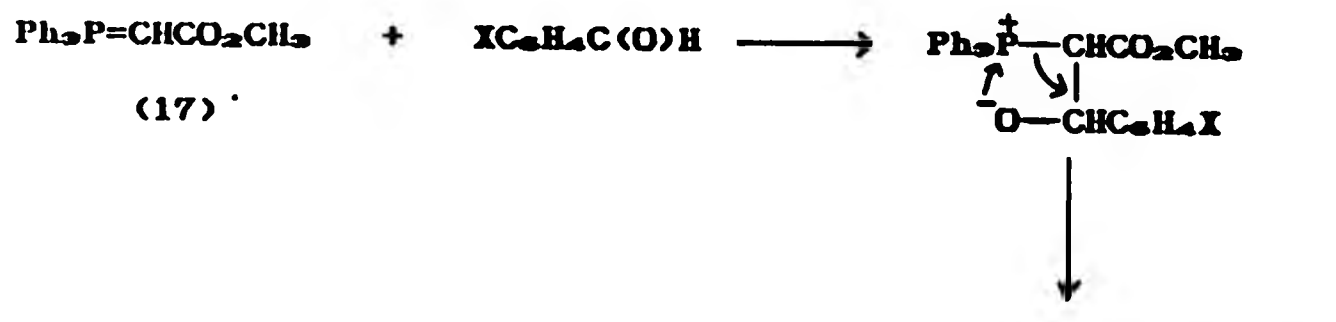
Attack on carbonyl oxygen [Scheme 4 (iv)] as a direct route to vinyloxyphosphonium salt has been suggested by several authors,[17,18] but comparison between the reactivity of triphenylphosphine and trimethyl phosphite towards α-chlorocyclohexane by Chopard *et al.*,[18] argues against such a mechanism. Hashimota and Furukawa[19] recently postulated this mechanism in the reaction of triethyl phosphite with phenacyl benzoates which gave exclusively the vinyl phosphate. No compelling evidence for this mechanism has been advanced.

Attack on the halogen [Scheme 4 (ii)] to form a halogenophosphonium enolate ion-pair (12), which rearranges to yield the Arbuzov and Perkow intermediates, or attack on carbonyl carbon [Scheme 4 (iii)] to form the betaine (8), which rearranges to yield the Arbuzov and Perkow intermediates (Scheme 6), are the most likely routes if a common intermediate is involved. However, in view of the experimental results obtained by several authors,[12-14] attack of the phosphorus atom at carbonyl carbon was postulated as the initial reaction step. The large negative entropies of activation, the Hammett ρ data and the solvent effect obtained from the reaction of trialkyl phosphite with aryl-substituted α-haloacetophenones are consistent with a



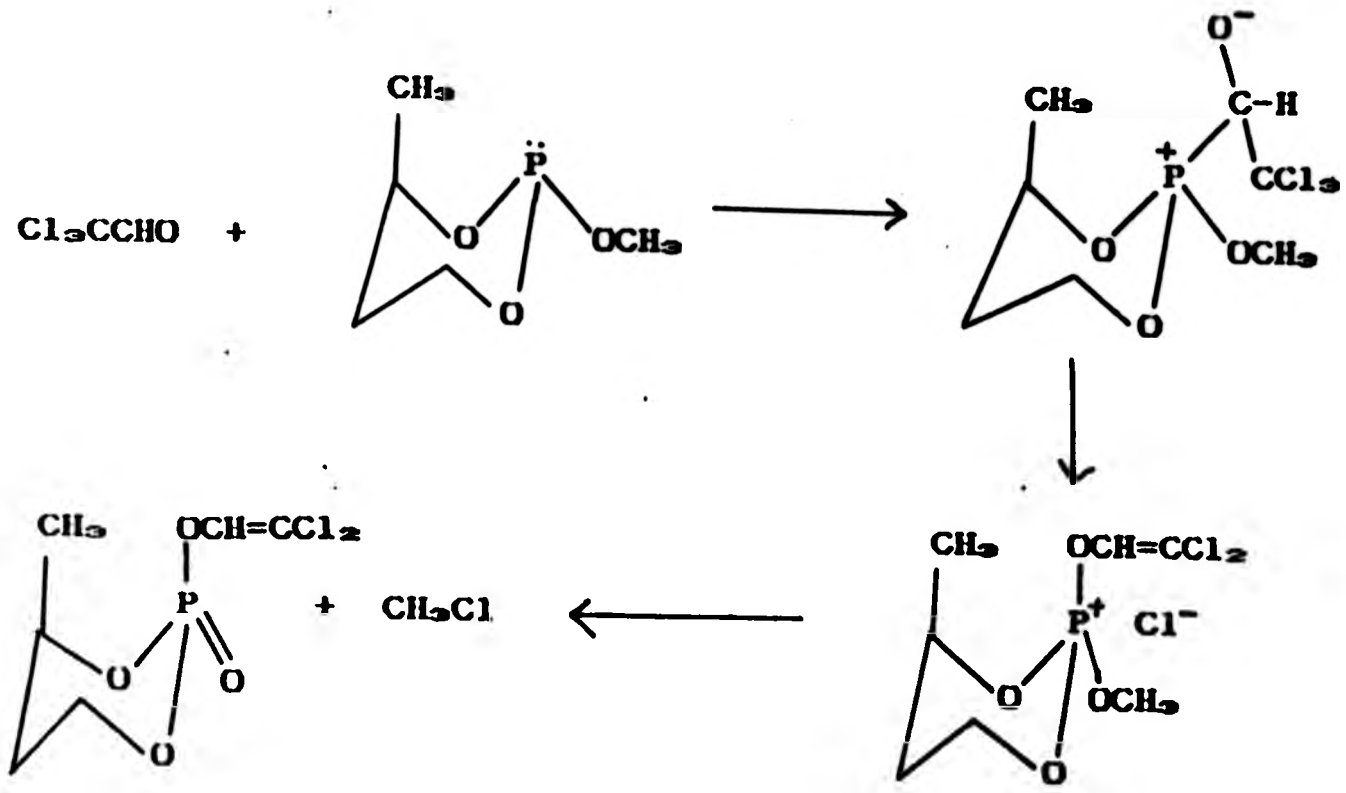
(Scheme 6)

polar and highly ordered transition state similar to that observed by Speziale *et al.*,[20] for the rate-determining nucleophilic addition of triphenylphosphonium-carbomethoxymethylide (17) to the carbonyl group of substituted benzaldehydes.



Amongst evidence put forward against the enolate ion-pair pathway by Borowitz[14] and Hudson[12] *et al.*, are the observations that: high yields of vinyl phosphate are obtained from both chloro- and bromo-ketones in hydroxylic solvents; acetic acid enhances the formation of vinyl phosphate from α-bromoketones at the expense of the ketophosphonate; the rate of reaction of α-chloroisobutyrophenones is increased in acetic acid and dehalogenation does not occur in spite of the sensitivity of the ion-pair to hydroxylic molecules. The concept of rate-determining nucleophilic addition to carbonyl carbon, as against halogen attack, is also supported by the work of Denney *et al.*,[21] who studied the reactions of a series of acyclic and cyclic phosphites with chloral (Cl_3CCHO) and ω,ω,ω-trichloroacetophenone (Cl_3CCOPh). Reaction with chloral was stereospecific and occurred with retention of configuration at phosphorus (Scheme 7). The stereochemical evidence precludes nucleophilic attack at the halogen for which inversion would be expected.

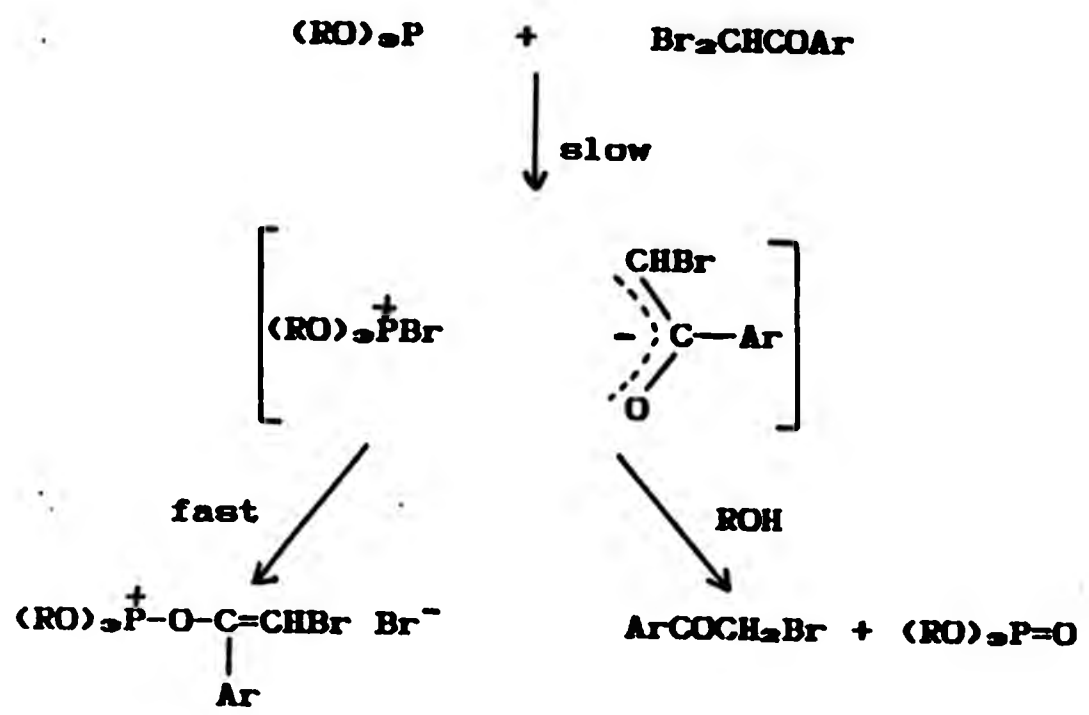
Contrary to the nucleophilic attack at carbonyl carbon, Borowitz[14] and Mlotkowska[16] *et al.*, provide good evidence that attack at halogen atom may occur in the reactions of trialkyl phosphites with α,α-dibromoketones and α-bromoketones which are sterically hindered to attack at the carbonyl centre. The ion-pair thus formed can be subsequently transformed by ligand exchange in aprotic medium into enol quasiphosphonium salt (10) affording the

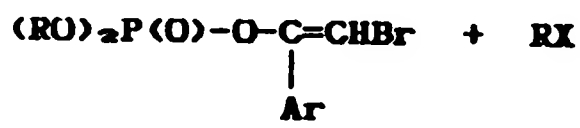


(Scheme 7)

corresponding enol phosphate (vinyl phosphate) by dealkylation. In protic solvents such ion-pairs undergo rapid solvolysis resulting in dehalogenation of the starting haloketone (Scheme 8).

The enhanced reactivity of 2,6-dichlorophenacylidene bromide (18) towards trialkyl phosphite compared to the chloride (19), the comparable reactivity of the bromide (18) and 2,4-dichlorophenacylidene bromide (20) towards

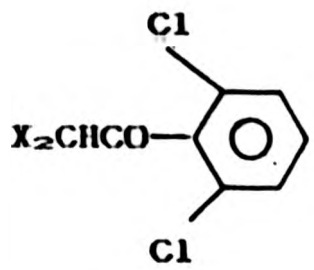




(Scheme 8)

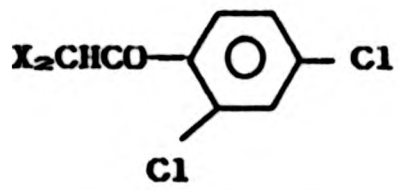
triethyl phosphite in spite of the considerably different steric hindrance, and the totally different reactivity of chloride (19) and 2,4-dichlorophenacylidene chloride (21) were interpreted by Borowitz's and Mlotkowska's *et al.*, in terms of different reaction mechanisms. The nucleophilic attack of the phosphite molecule is directed to the bromine atom in phenacylidene bromide and to the carbonyl centre in phenacylidene chloride. The increase in the quantity of the enol phosphate formed on exchanging from chlorine to bromine, in the reaction of 2,6-dichlorophenacyl chloride (22), and bromide (23) with trialkyl phosphites, was

interpreted also, in terms of different reaction mechanisms. In protic solvents the reaction course depends mainly upon the kind of halogen atom. Typical Perkow reactions or partial dehalogenation of the starting phenacylidene halides



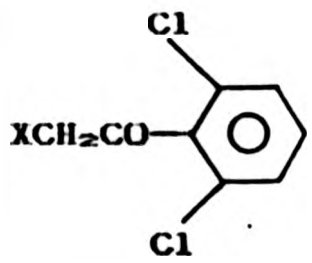
X = Br (18)

X = Cl (19)



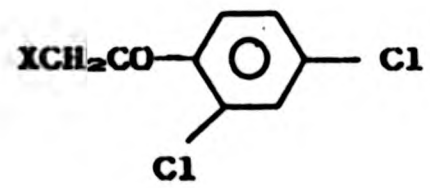
X = Br (20)

X = Cl (21)



X = Cl (22)

X = Br (23)



X = Br (24)

X = Cl (25)

are observed. Dehalogenation was found to be the predominant reaction in the reactions of 2,6-dichlorophenacyl bromide (23), and the bromides (18) and (20) with trimethyl phosphite in methanol, while 2,4-dichlorophenacyl chloride (25) and bromide (24) gave high yields of the vinyl phosphate with only a small quantity of dehalogenated products.

Chapter 2

DISCUSSION

2.1 Preparations of highly hindered alcohols and their phosphorus(III) esters.

In the interest of obtaining reaction intermediates (Perkow and Arbuzov) of greater stability, the preparations of highly hindered alcohols and their phosphorus(III) esters were investigated.

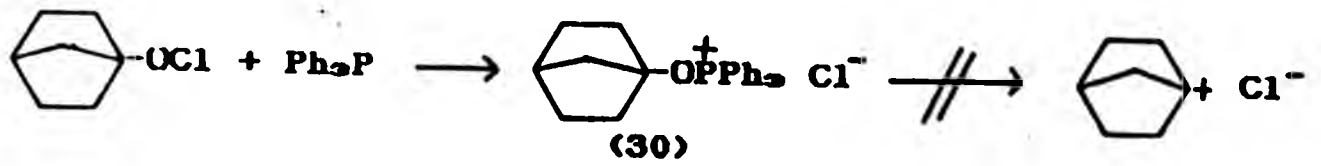
Phosphorus(III) esters derived from neopentyl alcohol have been used successfully in the isolation of some Arbuzov and Perkow intermediates.[12] The use of phosphorus(III) esters derived from 2,2-diethylbutan-1-ol (26) a slightly more hindered alcohol was therefore considered in the present work.

2,2,2-Triphenylethanol (27) had previously been used in the isolation of an intermediate *viz.* tri-n-butyl(2,2,2-triphenylethoxy)phosphonium bromide from the reaction of the alcohol (27) with tri-n-butylphosphine in the presence of bromine.[22] The successful isolation of the intermediate (28) was attributed to the difficulty of S_N2 displacement at a centre adjacent to a trityl group. The stabilising effect of the trityl group in the alcohol (27) led in the present work to the preparation and study of the reactions of its phosphorus(III) esters.

$$(C_6H_5)_3CCH_2OH + (n\text{-}C_4H_9)_3P + Br_2 \longrightarrow (C_6H_5)_3CCH_2O\overset{+}{P}(C_4H_9)_3\ Br^-$$

(27) (28)

The preparation and reactions of phosphorus(III) esters derived from norbornan-1-ol (29) was also suggested from the work of Denney,[23] who isolated norborn-1-yloxy(triphenyl)-phosphonium chloride (30) from the reaction of norborn-1-yl hypochlorite with triphenylphosphine. The failure of this reaction to give norborn-1-yl chloride as would be



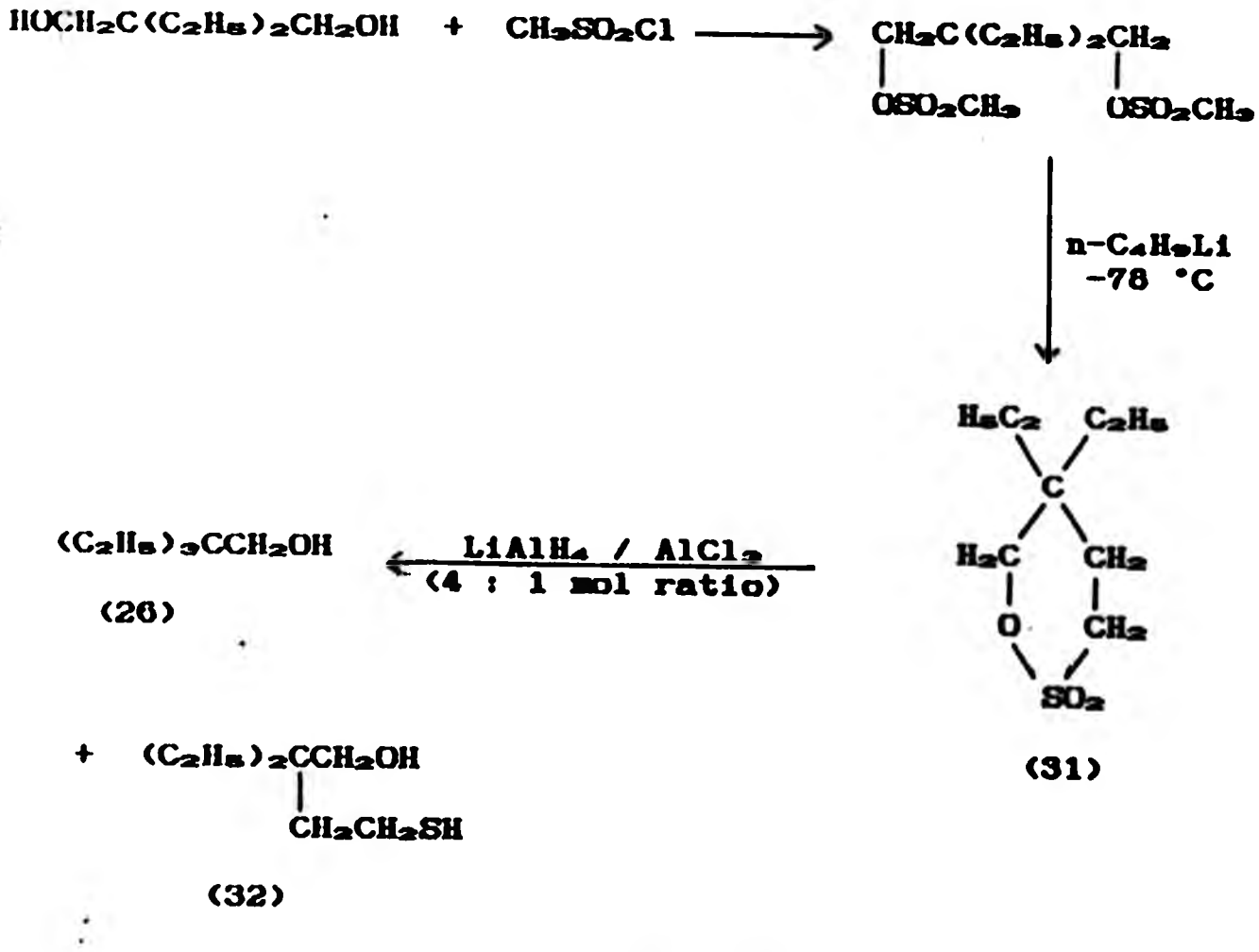
(30)

+ $Ph_3P=O$

expected by analogy with the reactions of acyclic systems,[24] was attributed to the failure of the brigehead carbon atom to undergo S_N1 and S_N2 reactions. The S_N2 pathway is forbidden, for clearly a nucleophile cannot approach the rear of the substituted carbon, nor can Walden inversion occur. The failure to undergo reaction by the S_N1 pathway easily is due to the steric requirement of carbonium ions, the rigid bicyclic structure constraining the ion to a non-planar geometry which is sufficiently unfavourable as to preclude reaction.

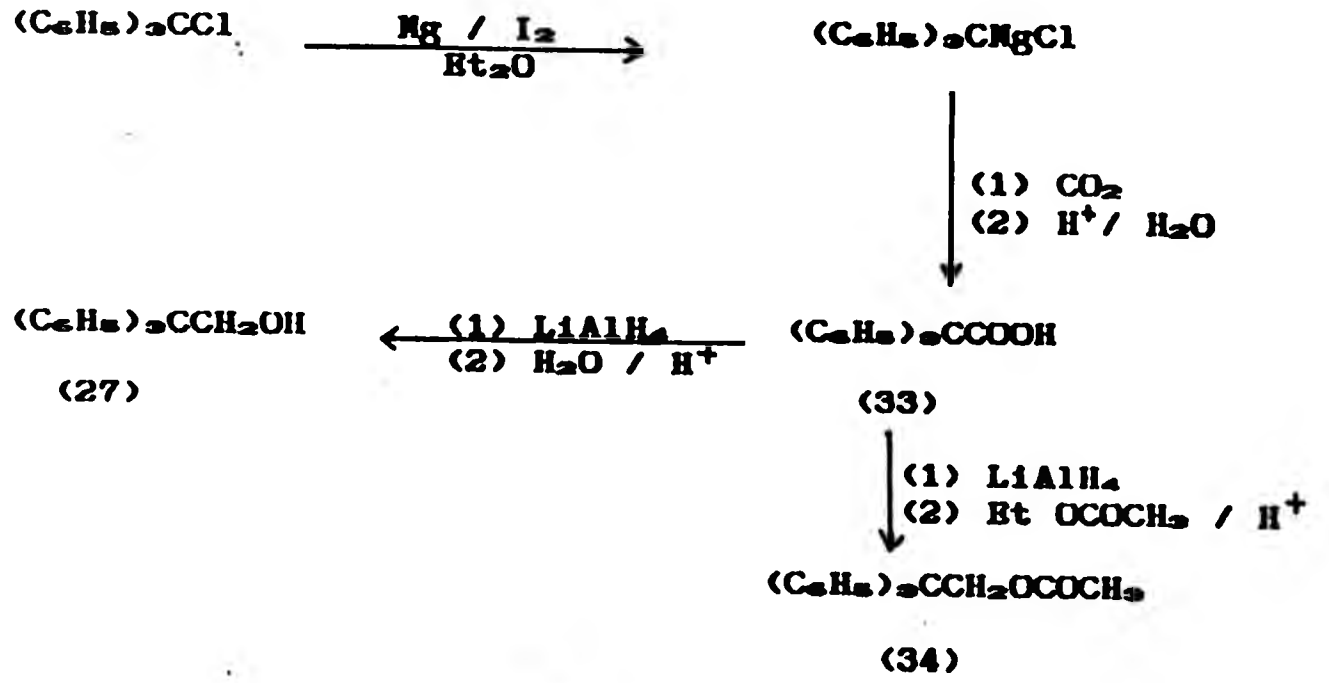
2.1.1 Preparation of alcohols: 2,2-diethylbutan-1-ol (26), 2,2,2-triphenylethanol (27), and norbornan-1-ol (29).

2,2-Diethylbutan-1-ol (26) was obtained from the aluminium hydride reduction of the sultone: 5,5-diethyl-1,2-oxathiane-2,2-dioxide (31) according to Smith and Wolinsky's method (Scheme 10).[28] The side product, 2,2-diethyl-4-mercaptobutan-1-ol (32) obtained was converted to the alcohol (26) by stirring in absolute alcohol with Raney nickel catalyst.



(Scheme 9)

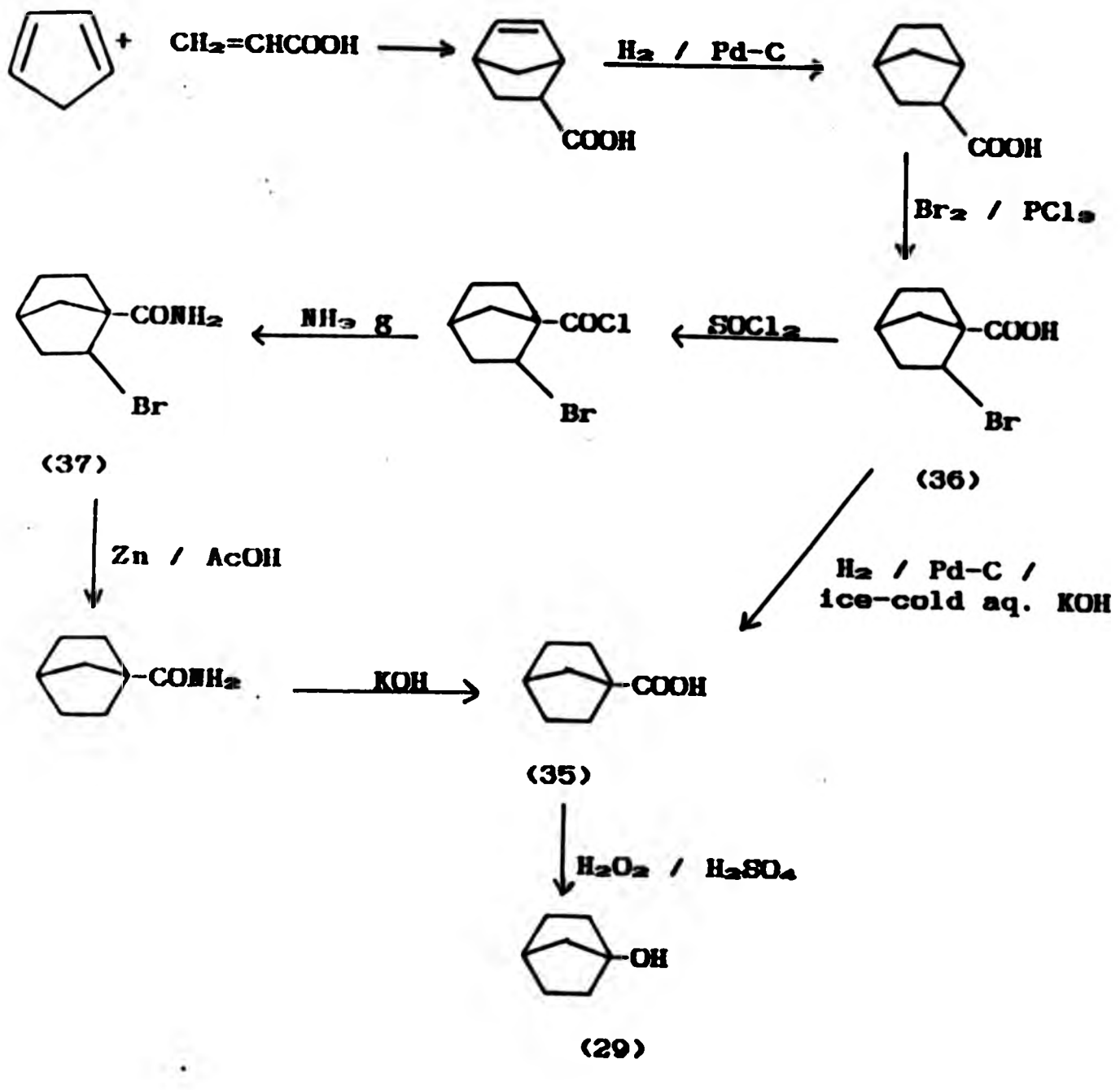
2,2,2-Triphenylethanol (tritylmethanol, 27) was prepared by the lithium aluminium hydride reduction of the acid, 2,2,2-triphenylacetic acid (33), which was obtained according to Greene *et. al.*[26] procedure with slight modification (Scheme 10).



(Scheme 10)

In the course of reduction of the triphenylacetic acid with lithium aluminium hydride, it was discovered that whereas the removal of excess lithium aluminium hydride by the addition of water in tetrahydrofuran allows the desired product, 2,2,2-triphenylethanol, to be isolated, the use of ethyl acetate, a safer method in decomposing lithium aluminium hydride, leads to the formation of 2,2,2-triphenylethyl acetate (34) which can however be hydrolysed by aqueous alkali to give the required alcohol (27).

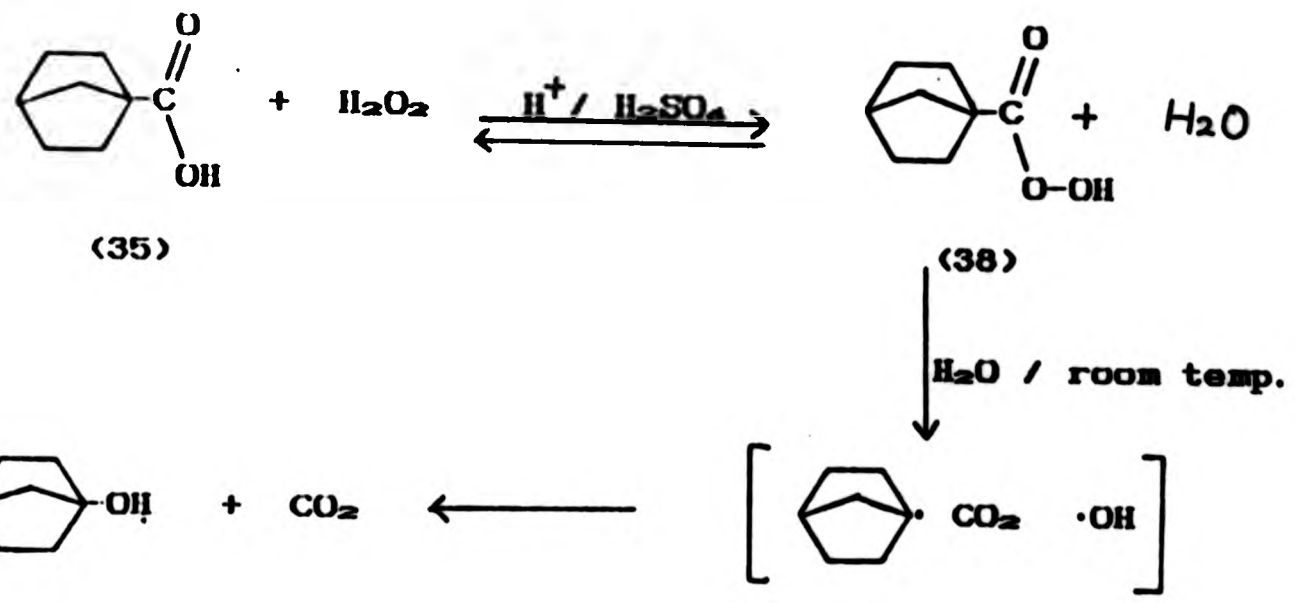
Norbornan-1-ol (29) was prepared by an oxidative cleavage of the acid norbornane-1-carboxylic acid (35) which was obtained as shown (Scheme 11). The formation of



(Scheme 11)

norbornane-1-carboxylic acid (35) from exo-2-bromo-norbornane-1-carboxylic acid (36) proceeded either by catalytic hydrogenation in the presence of ice-cold

potassium hydroxide or chemical reduction of the carboxamide (37) with zinc and acetic acid, followed by hydrolysis. In the course of reduction by catalytic hydrogenation it was found that, at room temperature the potassium hydroxide readily hydrolyses the bromocarboxylic acid (35) to a water soluble acid, probably exo-2-hydroxynorbornane-1-carboxylic acid. Norbornan-1-ol (29) was obtained from the acid (35) by an oxidative cleavage of the acid in the presence of 1.5 mole equivalent of 30 % v/v hydrogen peroxide and sulphuric acid (Scheme 12). The method involves formation of the peracid (38) which is stable below 0 °C and on stirring in ice-cold water decomposes probably by a free radical mechanism to give the alcohol (29) and carbon dioxide.



(29)

(Scheme 12)

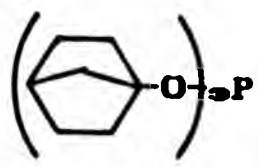
Norbornane, due to partial decomposition of the parent acid (35), was also obtained. On using the method of Della *et al.*[27] with a large concentration of hydrogen peroxide and stirring the resulting mixture at room temperature, only norbornane and the unchanged acid (35) were obtained. The mixture was also found to have solidified after adding about 5% of the required excess of hydrogen peroxide at -10 °C. The method of Parker *et al.*[28] for the direct preparation of aliphatic peracids containing six or more carbon atoms from the parent acids in the presence of 0.5 - 2.0 mole equivalent of hydrogen peroxide (50 - 65 % v/v) and concentrated sulphuric acid, was therefore used with modification. Since peracid formation is an equilibrium reaction (Scheme 12), the presence of a high amount of water (as in Della's[27] procedure with a large excess of 30 % v/v hydrogen peroxide) will shift the equilibrium back towards the parent acid which can then undergo partial decomposition to norbornane and carbon dioxide. Formation of the peracid was found to be very slow, with optimum yield of the alcohol being obtained when the mixture was left below 0 °C for 60 hours followed by stirring in ice-cold water for a further 5 hours.

2.1.2 Preparations and attempted preparations of phosphorus(III) esters, phosphates and phosphonates derived from the sterically hindered alcohols (26, 27 and 29).

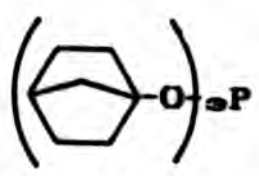
Phosphorus(III) esters: tris(2,2-diethylbutyl) phosphite (39), and trinorborn-1-yl phosphite (40) derived from 2,2-diethylbutan-1-ol, and norbornan-1-ol respectively, were prepared by the interaction of the appropriate molar ratio of the alcohol with phosphorus trichloride in the presence of *N,N*-dimethylaniline. Trinorborn-1-yl phosphate

$[(C_2H_5)_3CCH_2O]_3P$

(39)



(40)



(41)

(41) was prepared by oxidation of the phosphite (40) with t-butyl hydroperoxide. The oxidation was rapid with total conversion to the phosphate at room temperature after 1.5 hours.

Several attempts to prepare tris(2,2,2-triphenylethyl) phosphite (42) from 2,2,2-triphenylethanol (27) by the interaction of appropriate molar ratio of the alcohol (27) with phosphorus trichloride in the presence of *N,N*-dimethylaniline failed to give a significant amount of the ester (42). The dealkylated product, bis(2,2,2-triphenyl-ethyl) phosphite (43), was obtained as the major product

with α-phenylstilbene. Attempts to separate the trialkyl phosphite (42) present by distillation resulted in decomposition into the dialkyl phosphite (43) and α-phenylstilbene. The interaction of the alcohol (27) with phosphorus trichloride in the absence of a base was followed by ^{1}H n.m.r. (Scheme 13). Gradual formation of 2,2,2-triphenylethyl phosphorodichloridite (44) was observed

$$(C_6H_5)_3CCH_2OH + PCl_3 \longrightarrow (C_6H_5)_3CCH_2OPCl_2 + HCl \quad \ldots(1)$$

(44)

$$(C_6H_5)_3CCH_2OPCl_2 + (C_6H_5)_3CCH_2OH \longrightarrow [(C_6H_5)_3CCH_2O]_2PCl + HCl \quad \ldots(2)$$

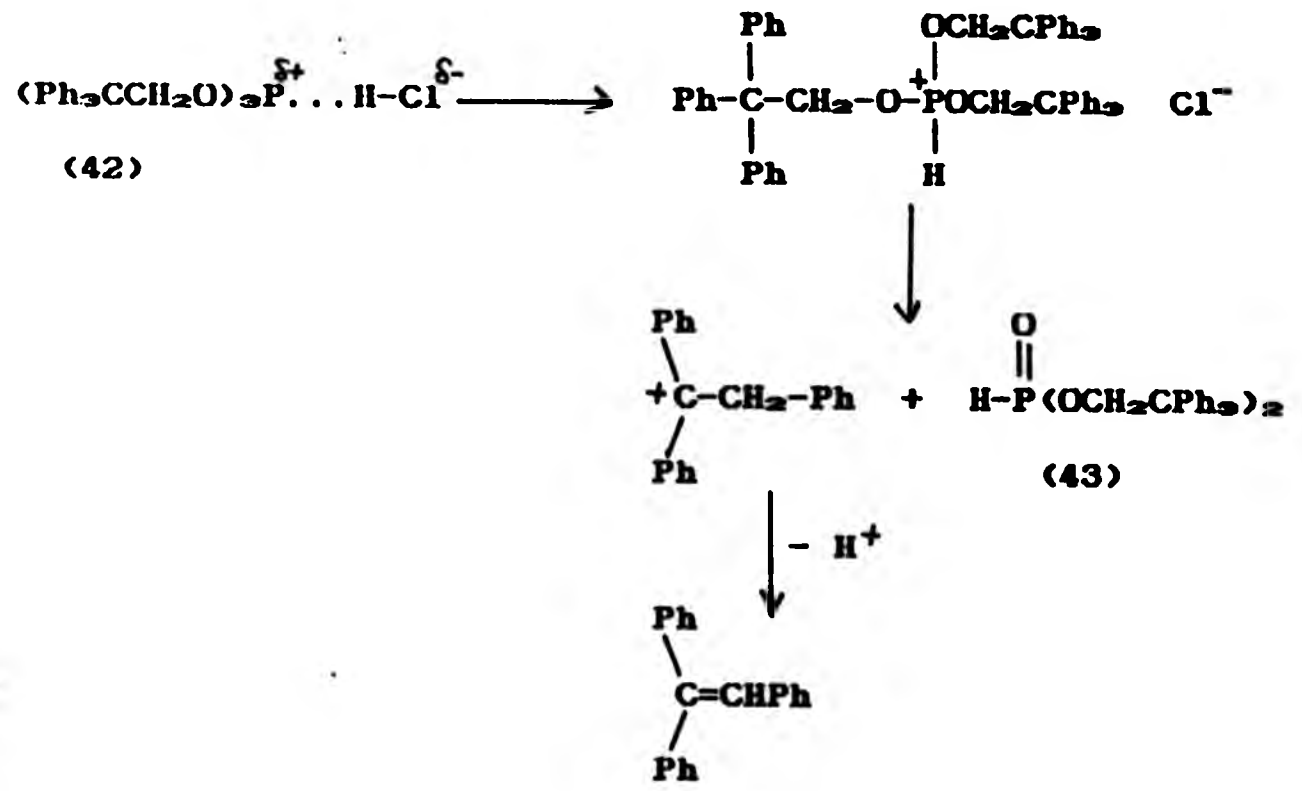
(45)

(Scheme 13)

in the first step, while in the second stage, formation of the bis(2,2,2-triphenylethyl) phosphorochloridite (45) was not observed; instead, the dialkyl phosphite (43) was obtained (see experimental page 131). ^{31}P n.m.r. after six weeks showed the mixture to contain the phosphoro-dichloridite (44) (*ca.* 34 mole %), and the dialkyl phosphite (43) (*ca.* 66 mole %).

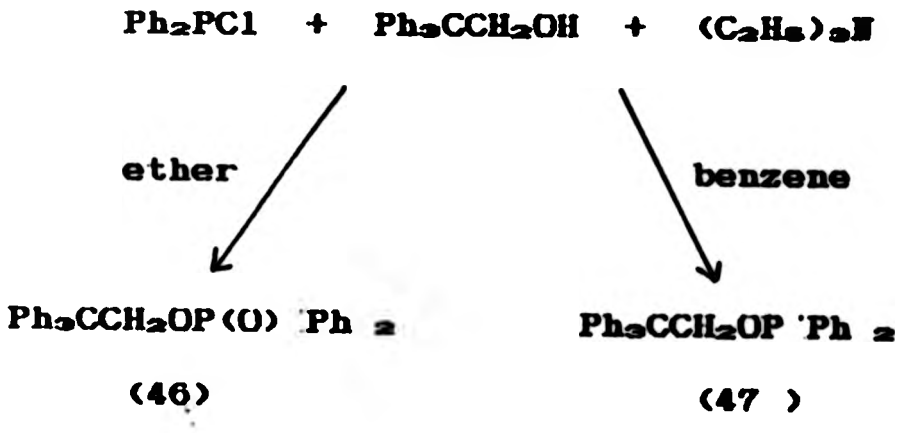
The ease of dealkylation of the trialkyl phosphite (42) and also possibly of the phosphorochloridite (45) by hydrogen chloride, despite the steric hindrance to S_N2 attack as compared to the trineopentyl and tris(2,2-

diethylbutyl) esters, was considered to be due largely to the participation of the phenyl ring in the rate-determining step and its greater migratory aptitude with the probable formation of a resonance stabilised carbonium ion intermediate (Scheme 14).[29]



(Scheme 14)

Reaction of chlorodiphenylphosphine with one mole equivalent of 2,2,2-triphenylethanol in anhydrous ether gave 2,2,2-triphenylethyl diphenylphosphinate (46) instead of the phosphinite (47) (Scheme 15). This unexpected result must have been caused by oxidation, probably by both peroxide present in the ether and aerial oxidation.



(Scheme 15)

The phosphinite (47) was however obtained when the reaction was carried out in benzene. Mixtures of unidentified compounds were also obtained in both reactions (see experimental page 134).

An attempt to prepare bis(2,2,2-triphenylethyl) phenylphosphonite (48) from dichlorophenylphosphine in the presence of triethylamine gave a mixture of unidentified compounds with ^{31}P chemical shift ranging from δ 26.6 to δ 9.7. The ^{31}P n.m.r. spectrum showed no signal assignable to the phosphonite (48) (with reference to dineopentyl phenylphosphonite δ_P 154)[2]

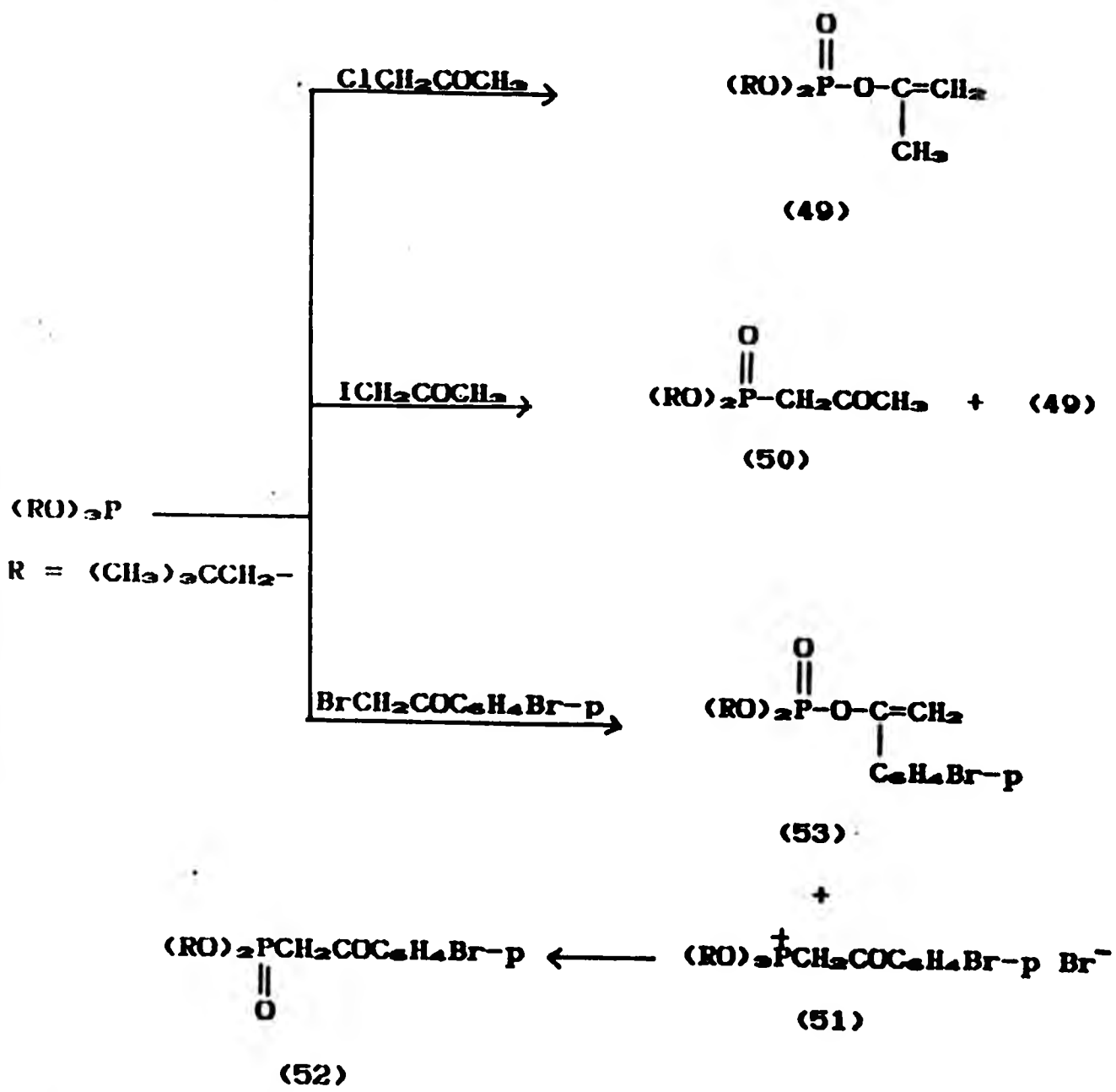
2.2 Interactions of trialkyl phosphites with α-haloketones.

Interactions of neopentyl phosphorus(III) esters with α-haloacetophenones have previously been shown to yield Michaelis-Arbuzov and Perkow intermediates (Scheme 5, page 15), which dealkylate to give the corresponding Michaelis-Arbuzov and Perkow products respectively. The present work was extended to studies of reactions of more highly hindered phosphorus(III) esters *viz.* tris(2,2-diethylbutyl) phosphite (39) and trinorborn-1-yl phosphite (40), and to a reinvestigation of the reactions of trineopentyl phosphite with other α-haloketones, in an attempt to isolate more stable Arbuzov and Perkow intermediates. The reactions were followed by ^{31}P and ^{1}H n.m.r. spectroscopy which enabled the various species present to be identified by their characteristic signals, in deuterochloroform at ambient temperature. Variations in the spectroscopic data obtained for the various compounds are discussed in Section 2.9.

Reactions of trineopentyl phosphite:

Interaction of trineopentyl phosphite with chloroacetone yielded the corresponding Perkow product, dineopentyl

1-methylvinyl phosphate (49) as the only product. In contrast, iodoacetone gave both the Arbuzov product, dineopentyl acetonylphosphonate (50) and the Perkow product (49) (Scheme 16). Reaction intermediates were not detected. Failure to detect the Arbuzov intermediate, may result in this case from the higher nucleophilicity of I- as compared



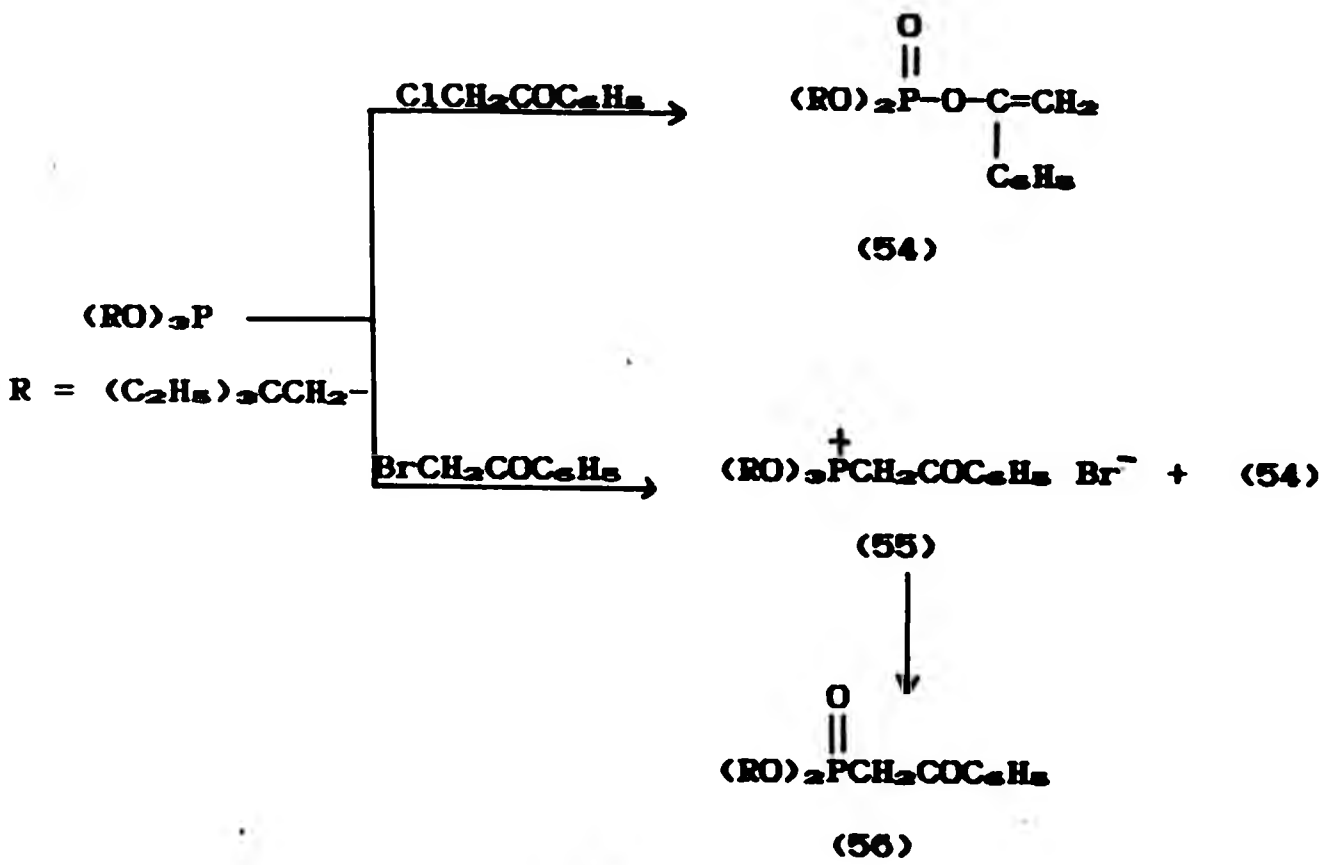
(Scheme 16)

to Br^- which was present in previously isolated examples from α-bromoacetophenone. In the interaction with α-bromo-p-bromoacetophenone, the ketophosphonium bromide (51) (Scheme 16) was identified as an intermediate of the Arbuzov reaction by its ^{31}P n.m.r. signal (δ_P 39.8). The final reaction mixture contained both the Arbuzov product, dineopentyl p-bromophenacylphosphonate (52), δ_P 18.9, and the Perkow product, dineopentyl 1-(p-bromophenyl)vinyl phosphate (53), δ_P -6.2. Although both the Arbuzov and Perkow routes were followed, the Perkow intermediate was too unstable for detection.

As was observed in previous studies,[12] the ketophosphonium bromide (51) that formed initially, gradually decomposed to the Arbuzov product (52) during the course of the reaction, while the Perkow product (53) was formed from the beginning. In all cases, the alkyl halide by-product was shown to consist exclusively of the neopentyl isomer $(CH_3)_3CCH_2X$ (X = Cl, I, Br), from which it can be concluded that the mechanism of alkyl oxygen fission involves no carbonium ion intermediate and that the S_N2 mode of reaction is in operation for dealkylation of the alkyloxyphosphonium species.

Reactions of tris(2,2-diethylbutyl) phosphite:

Interaction of tris(2,2-diethylbutyl) phosphite with α-chloro- and α-bromo-acetophenone followed the same pattern as that observed by Hudson *et al.*,[12] for trineopentyl phosphite. Reaction with α-chloroacetophenone followed the Perkow route only, to give the product bis(2,2-diethylbutyl) 1-phenylvinyl phosphate (54), δ_P -6.0, with no intermediate detected (Scheme 17). The reaction with α-bromoacetophenone

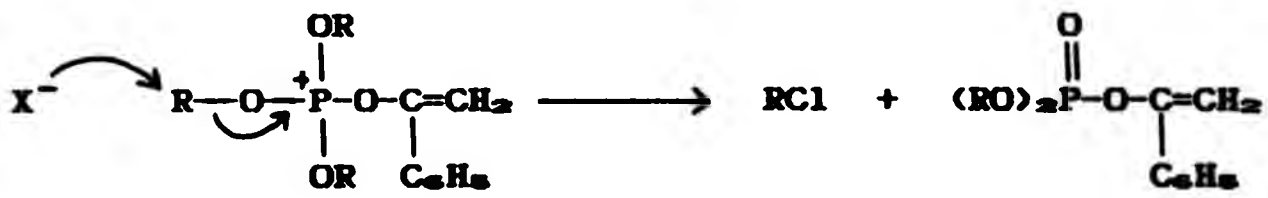


(Scheme 17)

followed both the Arbuzov and Perkow routes, with only the more stable Arbuzov intermediate, tris(2,2-diethylbutyloxy)-(phenacyl)phosphonium bromide (55), δ_P 40.7, detected

(Scheme 17). The Perkow route proceeds more rapidly to the Perkow product (54) while an initial build-up in the concentration of the phosphonium bromide (55) for about 20 minutes was observed before a progressive decomposition to the Arbuzov product, bis(2,2-diethylbutyl) phenacyl-phosphonate (56), δ_P 19.7.

^1H n.m.r. of the mixture at the end of the reaction confirmed the presence of the vinyl phosphate (54) with a signal at δ_H 5.2 (m), due to the vinyl protons and the phosphonate (56) with a signal at δ_H 3.7 (d, $^2J_{H-P}$ 18.6 Hz) due to the phosphorus-bonded methylene protons. ^1H n.m.r. also showed the presence of only 2,2-diethylbutyl bromide or chloride (δ_H 3.2, s, CH_2Br; δ_H 3.3, s, CH_2Cl), with no rearranged isomers, as the by-products from the dealkylation stages indicative of an S_N2 type of dealkylation (Scheme 18).



R = $(C_2H_5)_3CCH_2-$ X = Cl, Br

(Scheme 18)

It is interesting that the increased bulk of the β-substituents in the 2,2-diethylbutyl group, compared to

those in neopentyl,[12] does not appear to increase resistance to S_N2 attack to any significant extent.

Reactions of trinorborn-1-yl phosphite:

Interaction of trinorborn-1-yl phosphite with α-haloketones (Scheme 19) afforded quasiphosphonium halides of very high stability, including the first example of a stable vinyloxyphosphonium (Perkow) intermediate to be obtained from a trialkyl phosphite. Decomposition to the corresponding vinyl phosphate and ketophosphonate at room temperature was not observed. The structures were further confirmed by Fast Atom Bombardment Mass Spectrometry, which showed the quasiphosphonium ion in the positive ion spectrum and by X-ray structural analysis. These are discussed in Section 2.9.

Reaction with α-bromoacetophenone at room temperature gave only the corresponding ketophonium bromide, trinorborn-1-yloxy(phenacyl)phosphonium bromide (57), while α-chloroacetophenone gave no reaction at room temperature. When the reaction with α-chloroacetophenone was carried out at 69 °C, the ketophosphonium chloride (58) was obtained together with trinorborn-1-yl phosphate (59), dinorborn-1-yl phosphite (60) and two unidentified compounds, δ_P 41.9, and -14.3. Similarly, no reaction was obtained with chloroacetone at room temperature, but when carried out at

$BrCH_2COC_6H_5$ / R_T → $(RO)_3\overset{+}{P}CH_2COC_6H_5\ Br^-$ (57), δ_P 27.1

$ClCH_2COC_6H_5$ / R_T → No reaction

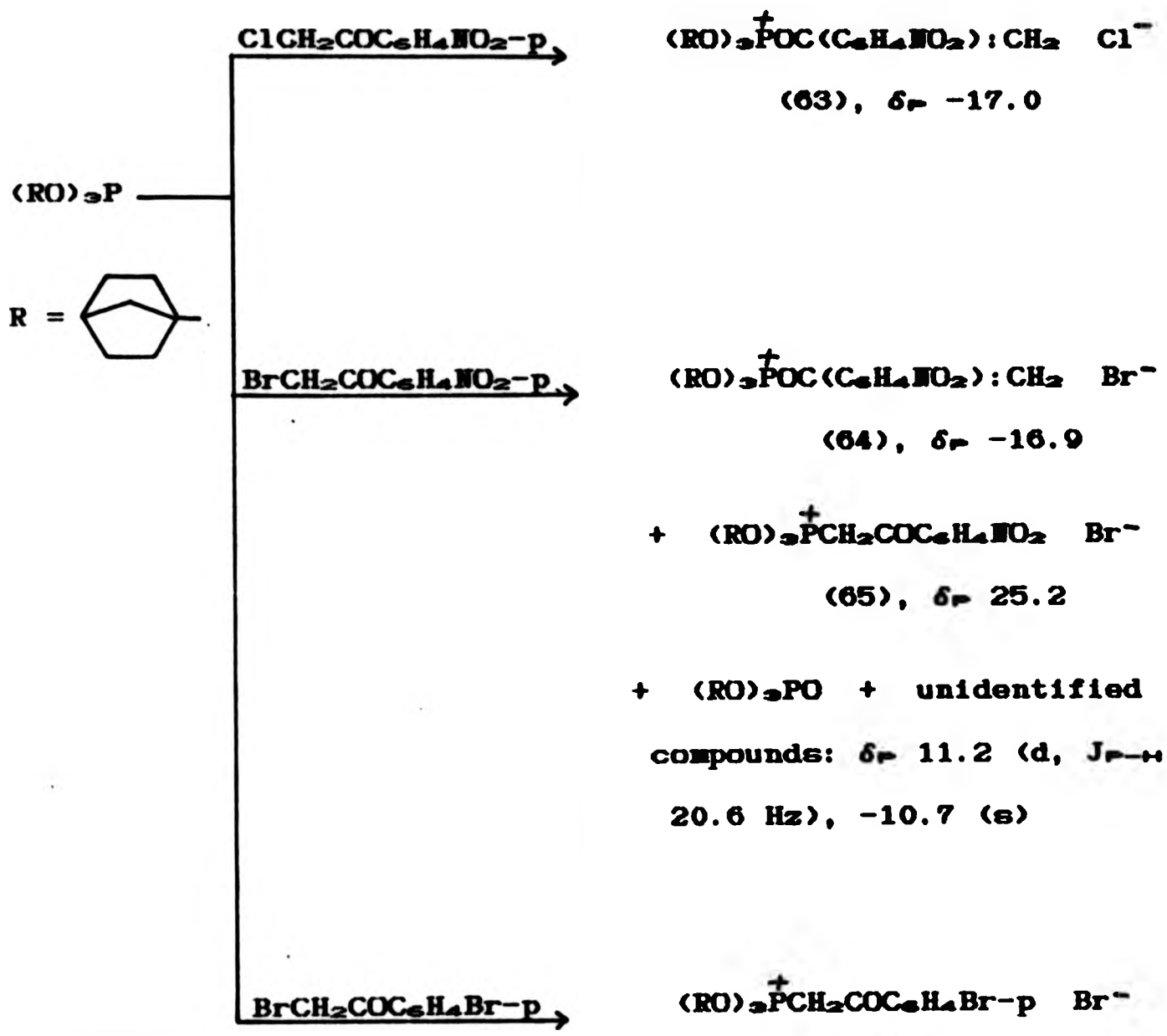
$ClCH_2COC_6H_5$ / 69 °C → $(RO)_3\overset{+}{P}CH_2COC_6H_5\ Cl^-$ (58), δ_P 26.7 + $(RO)_3PO$ (59), δ_P −10.4 + $(RO)_2P(O)H$ (60), δ_P −0.2 + unidentified compounds: δ_P 41.9 (s), −14.3 (s)

$(RO)_3P$, R =

$ClCH_2COCH_3$ / R_T → No reaction

$ClCH_2COCH_3$ / 69 °C → $(RO)_3\overset{+}{P}CH_2COCH_3\ Cl^-$ (61), δ_P 26.4 + $(RO)_3\overset{+}{P}OC(CH_3){:}CH_2\ Cl^-$ (62), δ_P −16.9 + $(RO)_3PO$ + $(RO)_2P(O)H$ + unidentified compounds: δ_P 116.0 (s), 29.2 (d, J_{P-H} 24.0 Hz), 23.5 (d, J_{P-H} 24.0 Hz), −14.4 (s)

(Scheme 19)



(Scheme 19) continued

69 °C, both the ketophosphonium chloride, trinorborn-1-yloxy(acetonyl)phosphonium chloride (61) and the vinyloxyphosphonium chloride, trinorborn-1-yloxy-1-methylvinyloxyphosphonium chloride (62) were obtained,

together with trinorborn-1-yl phosphate, dinorborn-1-yl phosphite and four unidentified compounds, δ_P 116.0, 29.2, 23.5, and -14.4.

Reaction of the phosphite (40) with α-chloro-p-nitroacetophenone at room temperature gave exclusively the vinyloxyphosphonium salt, trinorborn-1-yloxy-1-(p-nitrophenyl)vinyloxyphosphonium chloride (63), as the first example of stable Perkow intermediate to be isolated in the reaction of a trialkyl phosphite. Reaction with α-bromo-p-nitroacetophenone gave both the vinyloxyphosphonium bromide (64) and the ketophosphonium salt, trinorborn-1-yloxy(p-nitrophenacyl)phosphonium bromide (65) together with trinorborn-1-yl phosphate and an unidentified compound, δ_P 11.2. The α-chloro-p-nitroacetophenone reaction appeared to be slightly slower, about 8 % of unreacted trinorborn-1-yl phosphite being present in the mixture after 23 hours of reaction time, while no phosphite was present after 24 hours in the reaction of α-bromoacetophenone.

α-Bromo-p-bromoacetophenone reacted with trinorborn-1-yl phosphite to give the ketophosphonium salt, trinorborn-1-yloxy(p-bromophenacyl)phosphonium bromide (66), only.

In none of the trinorborn-1-yl phosphite reactions, was the formation of an intermediate prior to the quasi-phosphonium salts observed.

The various reaction products obtained from the preceding section, with different α-haloketones and phosphorus(III) esters, especially in the case of trinorborn-1-yl phosphite, can best be explained in terms of independent reaction pathways to the Michaelis-Arbuzov and Perkow products with no common intermediate as previously postulated. The two probable pathways are, nucleophilic attack of the phosphite on the carbonyl carbon to form the betaine (8) which then rearranges to yield the Perkow intermediate only (Scheme 4, page 13), and nucleophilic attack on the α-carbon which directly yields the Arbuzov intermediate. α-Chloroketones undergo prefentially the Perkow reaction *via* the betaine (8) while α-bromoketones can undergo both the Arbuzov and Perkow reactions. The ability of the α-bromoketones to undergo both reactions compared with α-chloroketones stems from the high polarizability of the carbon-bromine bond which facilitates the elimination of the bromide and thus favours nucleophilic attack of the phosphorus on the α-carbon atom.

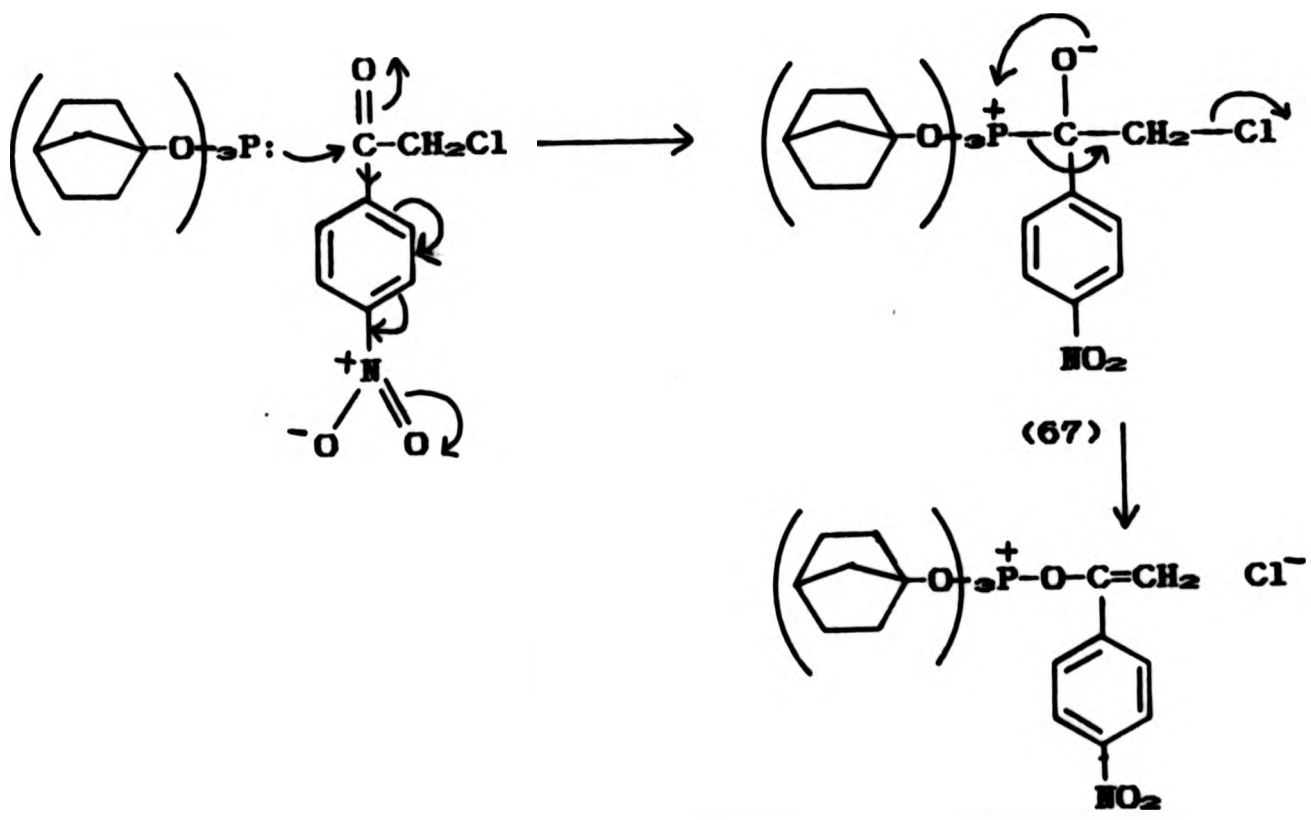
Attention has been paid by several workers,[14-16] to the reactions of less hindered trialkyl phosphites of relatively strong nucleophilicity such as trimethyl, triethyl, and tripropyl, with sterically hindered α-haloketones in which bulky substituents are around the carbonyl centre and/or on the α-carbon. The investigations, however, have not included a study of the opposite effect of using more bulky phosphites of relatively weak nucleophilicity with less

hindered α-haloketones. With trinorborn-1-yl phosphite (40), both steric and electronic effects influence the relative rates of its reactions.

The effectiveness of a nucleophile depends on a number of factors, but primarily on its basicity, its polarizability and any conjugative effects with the nucleophilic centre (the α-effect).[20] In terms of electronic effect, excluding the steric effect, the α-effect is more important in determining the nucleophilic reactivities of trialkyl phosphites. Trinorborn-1-yl phosphite is a relatively weak nucleophile compared to triethyl phosphite and trineopentyl phosphite, in which the electron releasing effect of their alkyl groups enhances their nucleophilicity. With norbornyl, a brigehead bicyclic group, the inductive effect or mesomeric effect through the tertiary carbon is absent.[24] Trinorborn-1-yl phosphite will therefore be expected to be less reactive towards a carbonyl group, unless the activity of the carbonyl group is increased by the presence of a strong electron-withdrawing group. Attack on the α-carbon carrying a highly polarized halogen, and activated by the carbonyl group, will be fairly accessible.

The failure of trinorborn-1-yl phosphite to react with α-chloroacetone and α-chloroacetophenone at room temperature, while α-chloro-p-nitroacetophenone reacted to give the vinyloxyphosphonium chloride (63), and also, the reaction of α-bromoacetophenone and α-bromo-p-bromo-

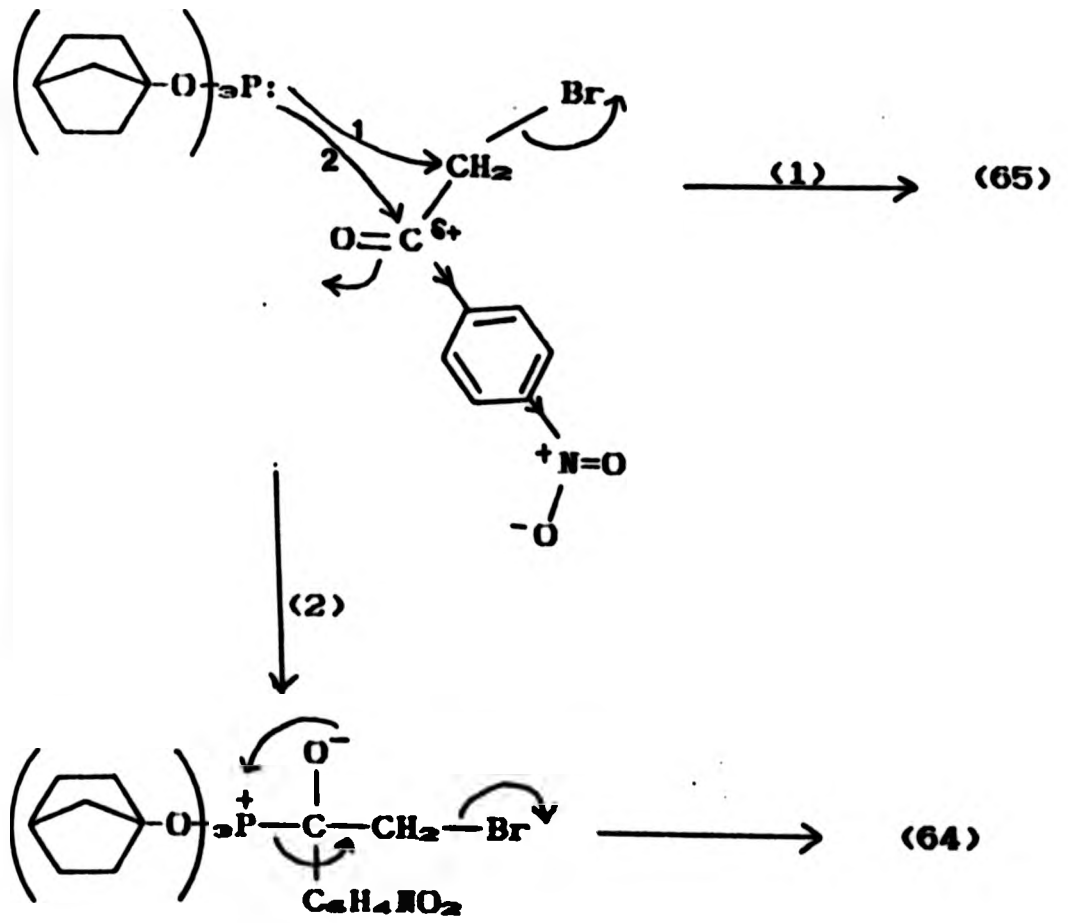
acetophenone to give only the ketophosphonium salts (57) and (66) respectively, could be explained in terms of the weak nucleophilicity of trinorborn-1-yl phosphite. Attack on the carbonyl carbon of chloroacetone, α-chloro-, α-bromo- and α-bromo-p-bromo-acetophenones is thus inhibited. The presence of a para substituted nitro group in the phenyl ring greatly increases the electrophilic character of the carbonyl carbon thereby facilitating the ease of nucleophilic attack (Scheme 20). The low polarizability of the carbon-chlorine bond



(Scheme 20)

prevents the attack on the α-carbon while the highly polarizable carbon bromine bond, facilitates the nucleophilic attack on the α-carbon of α-bromo- and α-bromo-p-bromo-acetophenones (Scheme 20).

The different reaction pathways to the Arbuzov and Perkow intermediates are both exemplified in the reaction of α-bromo-p-nitroacetophenone, which gave both the vinyloxy-phosphonium (64) and the ketophosphonium (65) bromides (Scheme 21). This is in contrast to the α-chloro- analogue and α-bromoacetophenone which each followed one pathway only (Scheme 20).



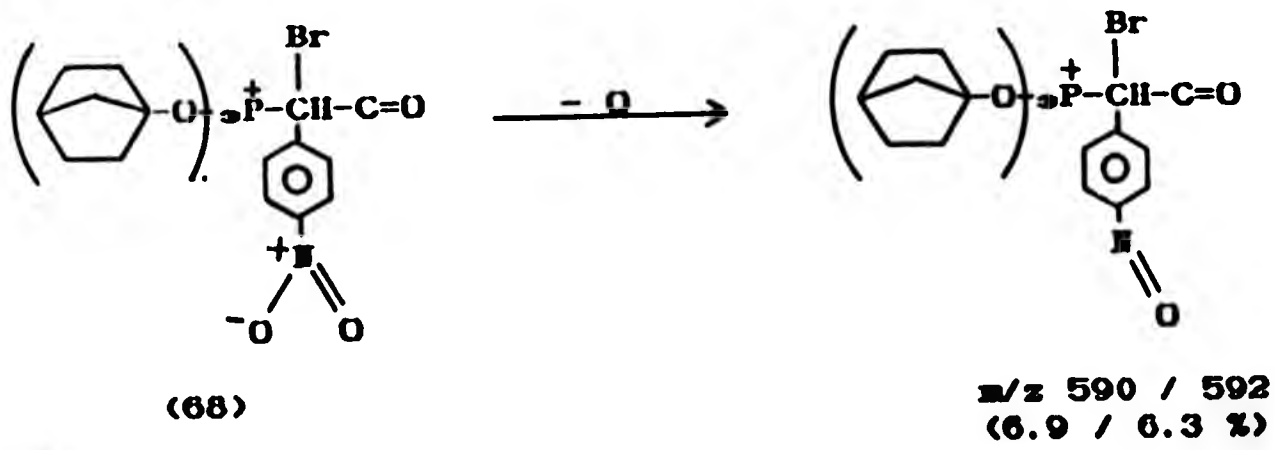
(Scheme 21)

Formation of both the vinyloxyphosphonium and ketophosphonium chlorides in the reactions of chloroacetone and α-chloroacetophenone is unusual. A higher reaction temperature is necessary, to overcome the increased activation energy for formation of the vinyloxyphosphonium chloride from trinorborn-1-yl phosphite, and the formation of the ketophosphonium chloride may also, therefore become more favourable. It is known that the ratio of ketophosphonate-vinyl phosphate generally increases with increasing temperature.[6] Though vinyloxyphosphonium chloride was not observed in the α-chloroacetophenone reaction mixture, evidence for its transitory formation was obtained from the detection of trinorborn-1-yl phosphate and phenylacetylene to which it decomposed rapidly, due to its instability at the reaction temperature. This represents an abnormal cleavage of the Perkow intermediate in which the vinyl grouping is preferentially removed and was also shown to occur in the decomposition of trinorborn-1-yloxy-1-(p-nitrophenyl)vinyloxyphosphonium chloride (63) (see section 2.6).

When the Arbuzov or Perkow route only was followed, as in the reaction of α-bromoacetophenone, and α-chloro-p-nitroactophenone with trinorborn-1-yl phosphite, the respective intermediate was obtained with no side product. However, additional side products were obtained when both routes occurred together, as in the reaction with α-bromo-p-

nitroacetophenone: (δ_P 11.2, d, J_{P-H} 20.6 Hz; δ_P -10.7, s), chloroacetone: (δ_P 116.0, s; δ_P 29.2, d, J_{P-H} 24 Hz; δ_P 23.5, d, J_{P-H} 24 Hz; δ_P -14.4, s), and α-chloroacetophenone: (δ_P 41.9, s; δ_P -14.3, s).

The additional product in the α-bromo-p-nitroacetophenone reaction, resonating at δ_P 11.5, and with a P-H coupling indicating a P-CH bond, was suspected to be an α-halogeno substituted β-ketophosphonium salt, trinorborn-1-yloxy(α-bromo-p-nitrophenacyl)phosphonium bromide (68). Evidence for the structure was supported by Fast Atom Bordardment mass spectroscopy of the reaction mixture, which showed the presence of an ion at m/z 590 / 592 indicating the presence of bromine in the compound, and the fragment corresponding to the loss of oxygen from the nitro group in the phosphonium bromide (68) (Scheme 22). This type of oxygen loss was shown to occur in the fragmentation of the vinyloxyphosphonium chloride (63) (see section 2.9.2), and also in the fragmentation of other nitro derivatives.[31]

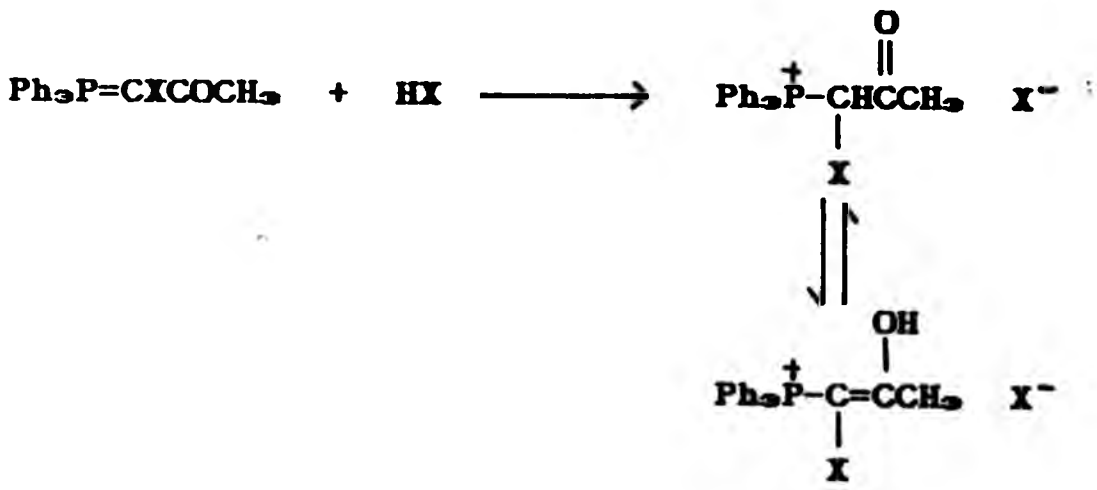


(68)

m/z 590 / 592
(6.9 / 6.3 %)

(Scheme 22)

The introduction of an electronegative atom into the α-position of a β-ketophosphonium salt would lead both to increase in the mobility of the hydrogen atom of the methylene group and also to increase in the acidity of the enol hydroxyl which should influence the degree of enolization of these compounds. Formation of the keto form of the phosphonium bromide (68) in the α-bromo-p-nitroacetophenone reaction, was in accord with the work of Aladzheva *et al.*,[32] on the tautomerism of α-halogeno-substituted β-ketophosphonium salts (Scheme 23). Aladzheva *et al.*,[32] found that the introduction of a chlorine atom

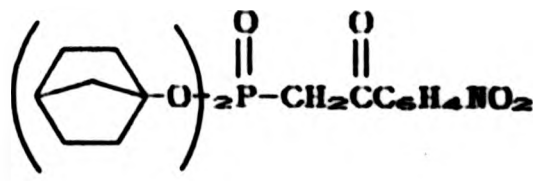


X = Cl, Br

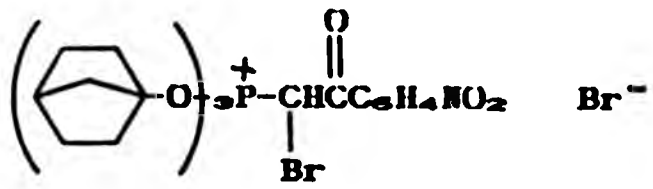
(Scheme 23)

into the α-position increases enolization, but the introduction of a bromine atom decreases enolization. ^{31}P n.m.r. of the decomposed mixture of the phosphonium salts obtained in the α-bromo-p-nitroacetophenone reaction (see

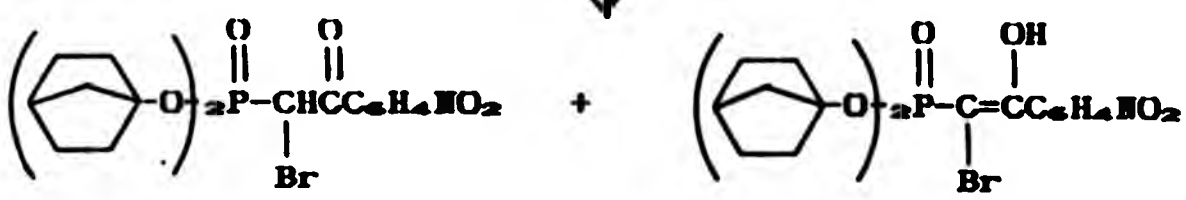
experimental page 145), showed the presence of dinorborn-1-yl p-nitrophenacylphosphonate (69) (δ_P 12.2), trinorborn-1-yl phosphate, and two unidentified compounds, δ_P 4.7 and δ_P 4.5, which could probably be attributed to both the keto and enol form of dinorborn-1-yl α-bromo-p-nitrophenacyl-phosphonate, (70) and (71) respectively (Scheme 24). The presence of the polarized P=O bond would further increase the mobility of the hydrogen atom of the methylene group.



(65)



(68)

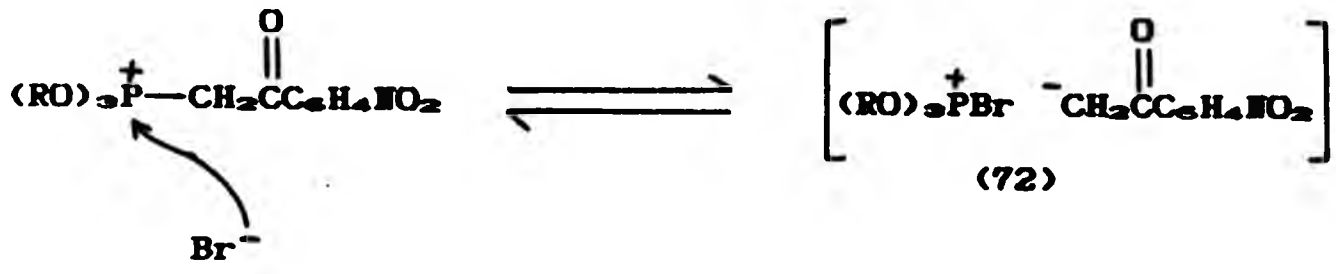


(70) (71)

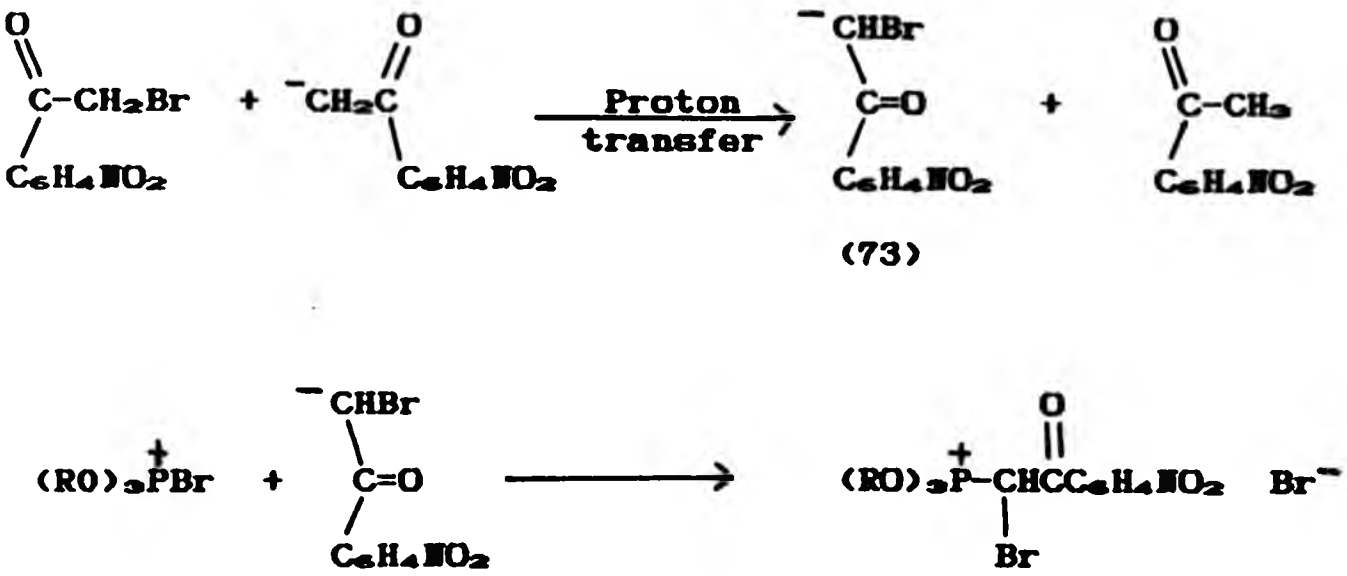
(Scheme 24)

The α-bromophenacylphosphonium bromide (68) could possibly be formed through an ion-pair intermediate (72)

(Scheme 25), formed by ligand exchange in the phenacylphosphonium bromide (57), to give a resonance stabilized p-nitroacetophenonyl anion. The latter could



(57) (72)



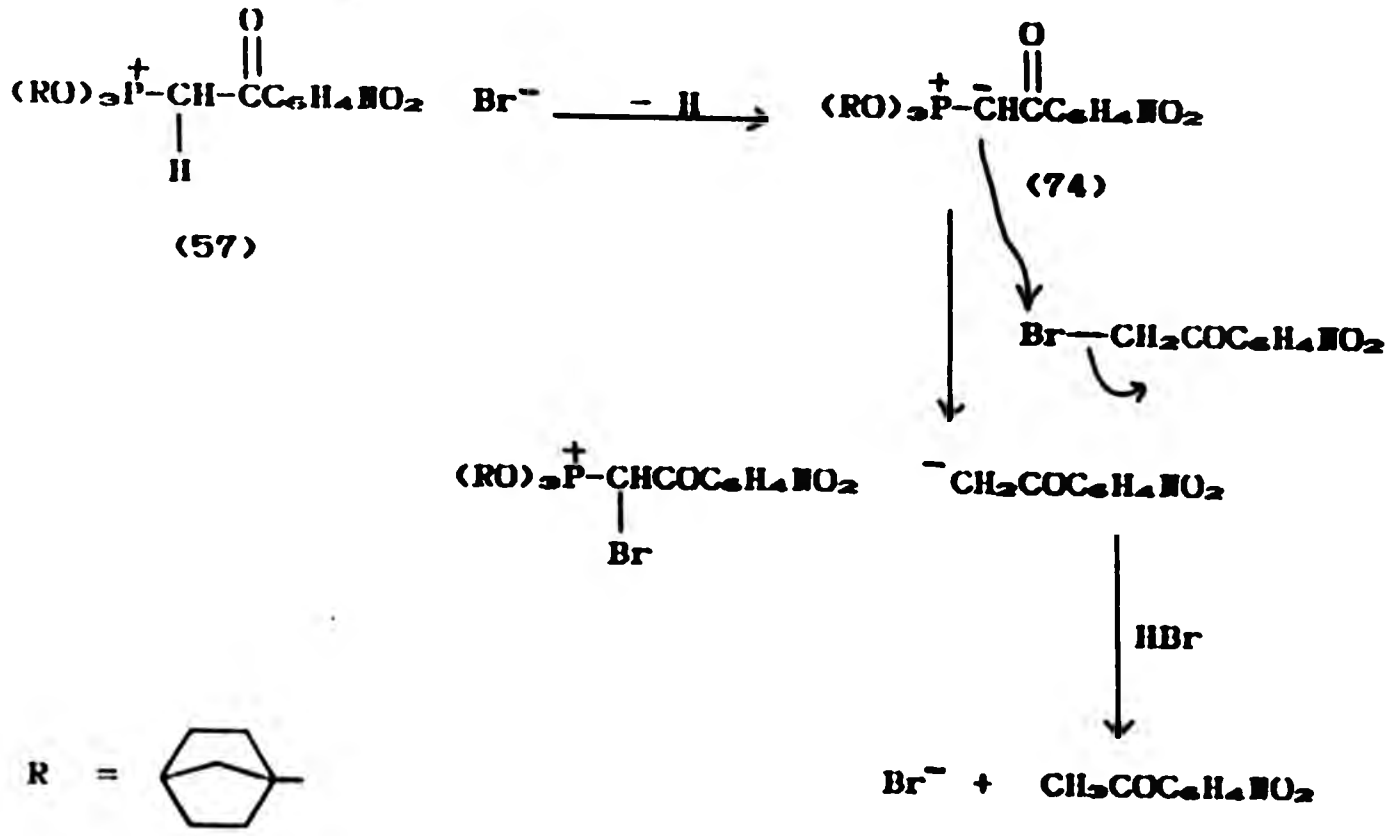
(73) (68)

(Scheme 25)

then undergo proton transfer from the starting α-bromo-p-nitroacetophenone, affording a new more stabilized anion (73), which finally reacts with the bromophosphonium cation

derived from the ion-pair (72) to give the α-bromophenacyl-phosphonium bromide (69).

Formation of the α-bromophenacylphosphonium bromide from the ylid (74) (Scheme 26), by reacting with a positive bromine source, such as the starting α-bromo-p-nitro-acetophenone, is also feasible.



(Scheme 26)

Trialkyl phosphites are known to take part in nucleophilic attack on acetylenes.[33] The additional side products obtained in the reactions of chloroacetone, and α-chloroacetophenone with trinorborn-1-yl phosphite, might possibly stem therefore from the reactions of the acetylenes, prop-1-yne, and phenylacetylene with the

phosphite. Prop-1-yne is formed from the decomposition of trinorborn-1-yloxy-1-methylvinyloxyphosphonium chloride (62) in the chloroacetone reaction, and phenylacetylene is formed from the decomposition of trinorborn-1-yloxy-1-phenylvinyl-oxyphosphonium chloride, in the chloroacetophenone reaction. The side products were however formed in too small quantities for their identification to be possible.

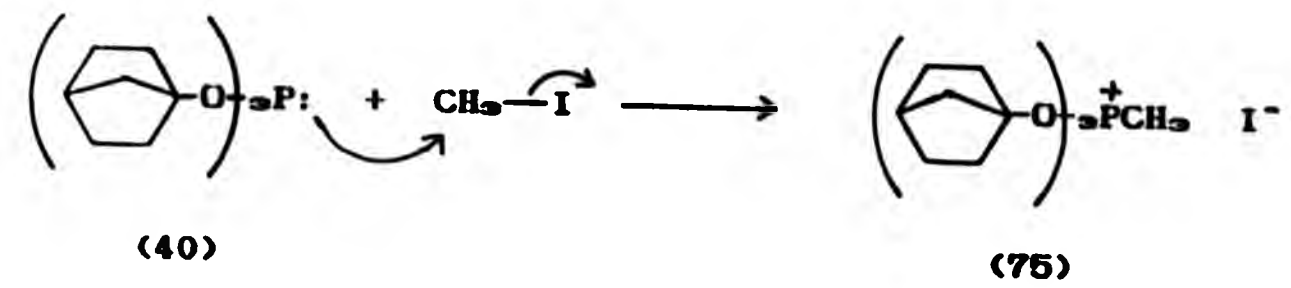
2.3 Interaction of trinorborn-1-yl phosphite (40) and 2,2,2-triphenylethyl diphenylphosphinite (47) with methyl iodide.

A number of stable Arbuzov intermediates have been obtained from phosphorus(III) esters with alkyl halide and the mechanisms of the reactions have been widely reviewed.[1] The present work was extended to the use of a new sterically hindered phosphite (40) and phosphinite (47).

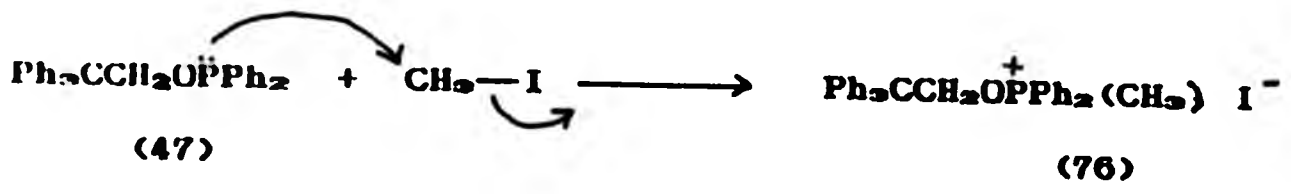
Trinorborn-1-yl phosphite (40) reacted with methyl iodide to give exclusively the phosphonium iodide, trinorborn-1-yloxy(methyl)phosphonium iodide (75) (δ_P 36.9), (Scheme 27), as a very stable salt and highly resistant to attack by atmosperic moisture. The rate of formation of the phosphonium iodide (75) was comparable with the rate at which the analogue, trineopentyloxy(methyl)phosphonium iodide was formed. This is in contrast to the observed reactivity of trinorborn-1-yl phosphite towards α-halo-ketones compared to the neopentyl analogue (section 2.2), which was explained in terms of the weak nucleophilicity of trinorborn-1-yl phosphite. The driving force in the reaction of trinorborn-1-yl phosphite with methyl iodide is the high polazability of the carbon-iodine bond, which facilitates the elimination of the iodide.

2,2,2-Triphenylethyl diphenylphosphinite (47) also gave the phosphonium salt, 2,2,2-triphenylethoxy(diphenyl)-methylphosphonium iodide (76), δ_P 72.7, (Scheme 27) as the

only compound. The phosphonium salt (76) was found to be stable at room temperature in the absence of moisture for about a week, after which decolouration of the salt from white to yellow was observed. The salt (76) solution in deutorochloroform was also stable for about 44 hours after which, it started decomposing to diphenyl(methyl)phosphine oxide. The surprising low stability of the phosphonium salt (76) compared to the neopentyl analogue,[2] may be due to the tendency of the 2,2,2-triphenylethoxy group to undergo S_N1 fission, facilitated largely by the participation of the phenyl ring in the rate determining step.



(40) (75)

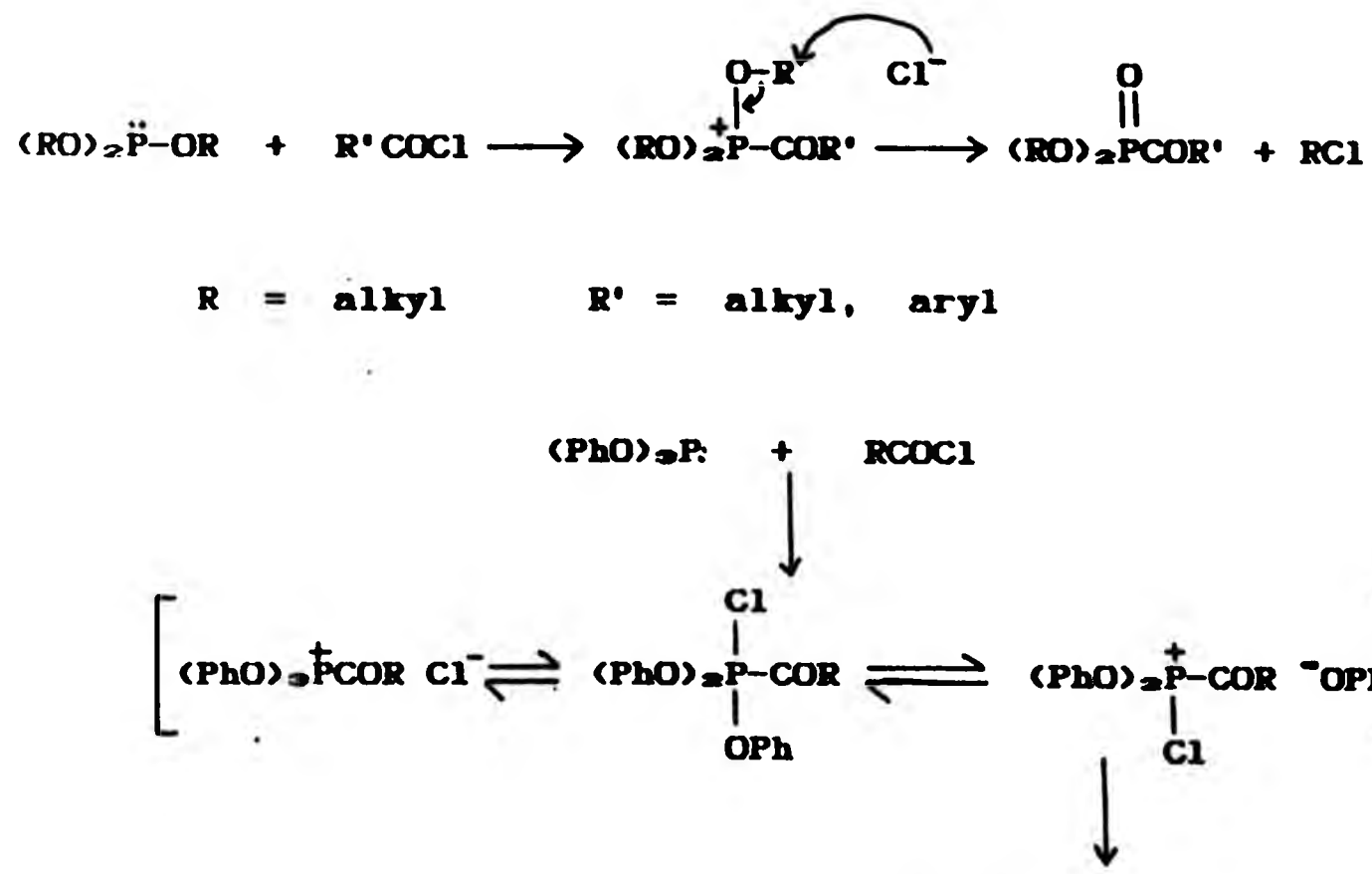


(47) (76)

(Scheme 27)

2.4 Interaction of trineopentyl phosphite and trinorborn-1-yl phosphite (40) with benzoyl chloride.

Reactions of acyl or simple aroyl chlorides with trialkyl phosphites have been found to proceed in accordance with the Michaelis-Arbuzov reaction leading to the formation of O,O-dialkyl acyl (or aroyl) phosphonates[5,34] (Scheme 28). However, triphenyl phosphite has been shown to react with the formation of the diphenyl phosphorochloridite and the phenyl carboxylate[34] (Scheme 28).

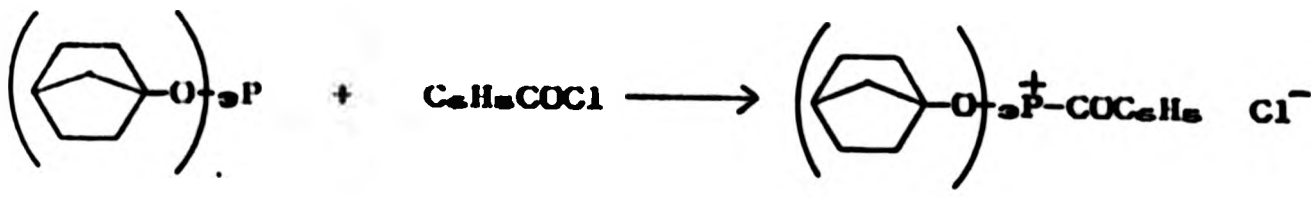


(Scheme 28)

In the present work, ^{31}P n.m.r. spectroscopy was used to investigate the reaction of trineopentyl phosphite and trinorborn-1-yl phosphite with benzoyl chloride at room temperature.

Reaction with trinorborn-1-yl phosphite was found to be very slow, about 88 % of the phosphite (46) remaining unreacted after 21 hours of reaction time. The ^{31}P n.m.r. spectrum of the reaction mixture after three months, showed a mixture of phosphorus-containing compounds to be present (see experimental page 156) with the major compound at δ_P -10.6 identified as trinorborn-1-yl phosphate formed by partial oxidation of the phosphite during the course of the reaction. Attempts to isolate any phosphonium salts that might be present in the mixture by trituration with anhydrous ether afforded a mixture of compounds resonating at δ_P: 31.7, 20.4, 15.7 and -14.2 .

Reaction of trinorborn-1-yl phosphite with benzoyl chloride would be expected to form the stable phosphonium salt, trinorborn-1-yloxy(benzoyl)phosphonium chloride (77),

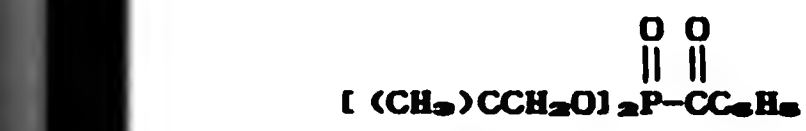


(77)

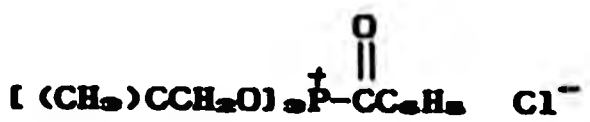
by analogy with the reactions of α-haloketones and methyl iodide (Scheme 19 and 27). In the absence of any data on the chemical shift for acylphosphonium salts with which to

compare the benzoylphosphonium chloride (77) shift, it is difficult to know whether any of the products might correspond to the phosphonium salt (77). The quantities of the products are too small for further characterization. It appears however, that the formation of the benzoyl-phosphonium salt (77) does not take place to any significant extent.

Interaction of trineopentyl phosphite with benzoyl chloride also gave a mixture of phosphorus-containing compounds. The reaction was relatively slow with about 27 % of unreacted phosphite remaining after 20 hours of reaction time. ^{31}P n.m.r. of the mixture after 3 months showed the presence of trineopentyl phosphate (δ_P -1.2), a signal at δ_P -1.8, which was assumed to be dineopentyl benzoyl phosphonate (78), based on diethyl benzoylphosphonate, δ_P -1.8,[38] and an unidentified compound, δ_P 16.4, as the major compounds. The Arbuzov intermediate, trineopentyloxy-(benzoyl)phosphonium chloride (79), appeared to be too



(78)



(79)

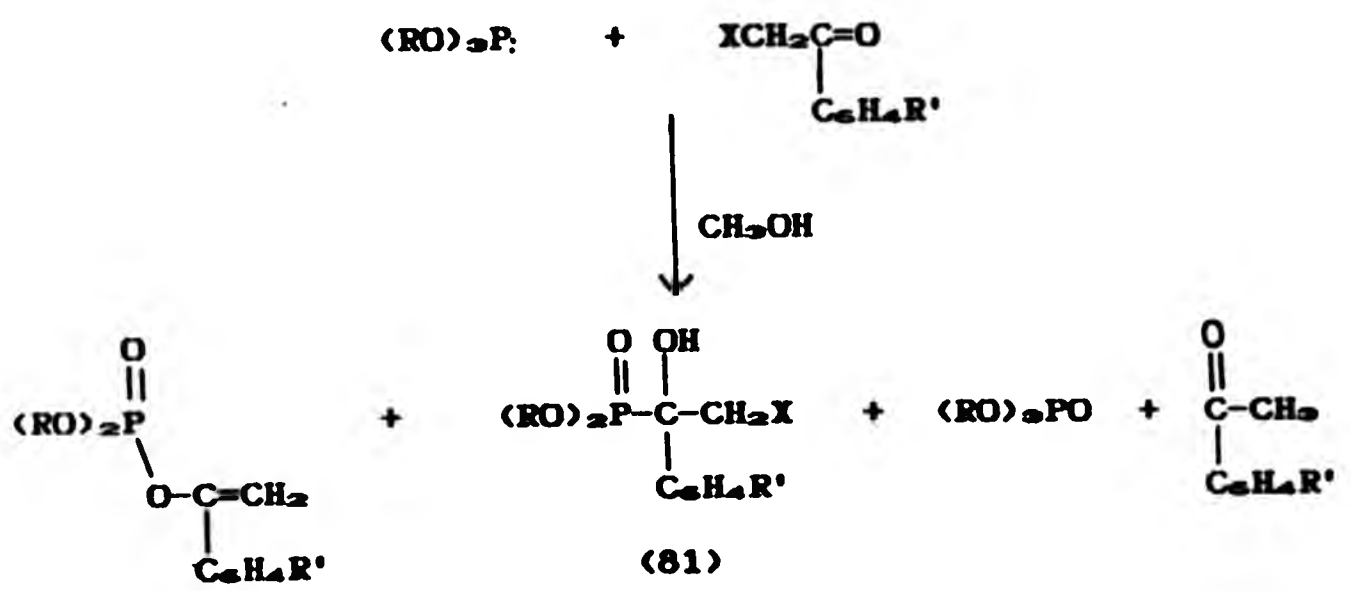
unstable for detection to occur, as any signal showing the usual initial build-up in concentration followed by decrease in concentration as the phosphonate (78) was formed (by analogy with the reaction of trialkyl phosphite with

α-bromoketones)[12] was not observed.

Reaction with trineopentyl phosphite proceeded by the Arbuzov reaction pathway (Scheme 28) to give the benzoylphosphonate (78). The presence of trineopentyl phosphate is probably due to a partial oxidation of the phosphite during the course of the reaction.

2.5 Interaction of trimethyl phosphite with α-chloroacetophenones in methanol.

As an extension of the work of Petnehazy *et al.*,[36] on the mechanistic interpretation of the products formed in the reactions of trialkyl phosphites with various substituted α-haloacetophenones in protic solvents (Scheme 29), the reactions of trimethyl phosphite with α-chloro-, α-chloro-p-chloro- and, α-chloro-p-nitroacetophenones were investigated by ^{31}P n.m.r. spectroscopy (gated decoupling) in order to ascertain the product composition, and the effect of excess trialkyl phosphite used by Petnehazy[36] on the products ratio.



(Scheme 29)

In the reaction of varying concentration of trimethyl phosphite with α-chloroacetophenone, a slight change on increasing the trimethyl phosphite - α-chloroacetophenone mole ratio from 1:1 to 10:1 was observed for the dimethyl α-hydroxyphenacylphosphonate (81) - dimethyl 1-phenylvinyl phosphate (80) (Scheme 29, R = CH_3, R' = H, X = Cl) product ratio, with the equilibrium favouring the α-hydroxyphenacyl-phosphonate, but a more definite swing in the favour of the vinyl phosphate (80) appeared to be formed at 20:1 mole ratio (Table 1). Similar results were obtained with

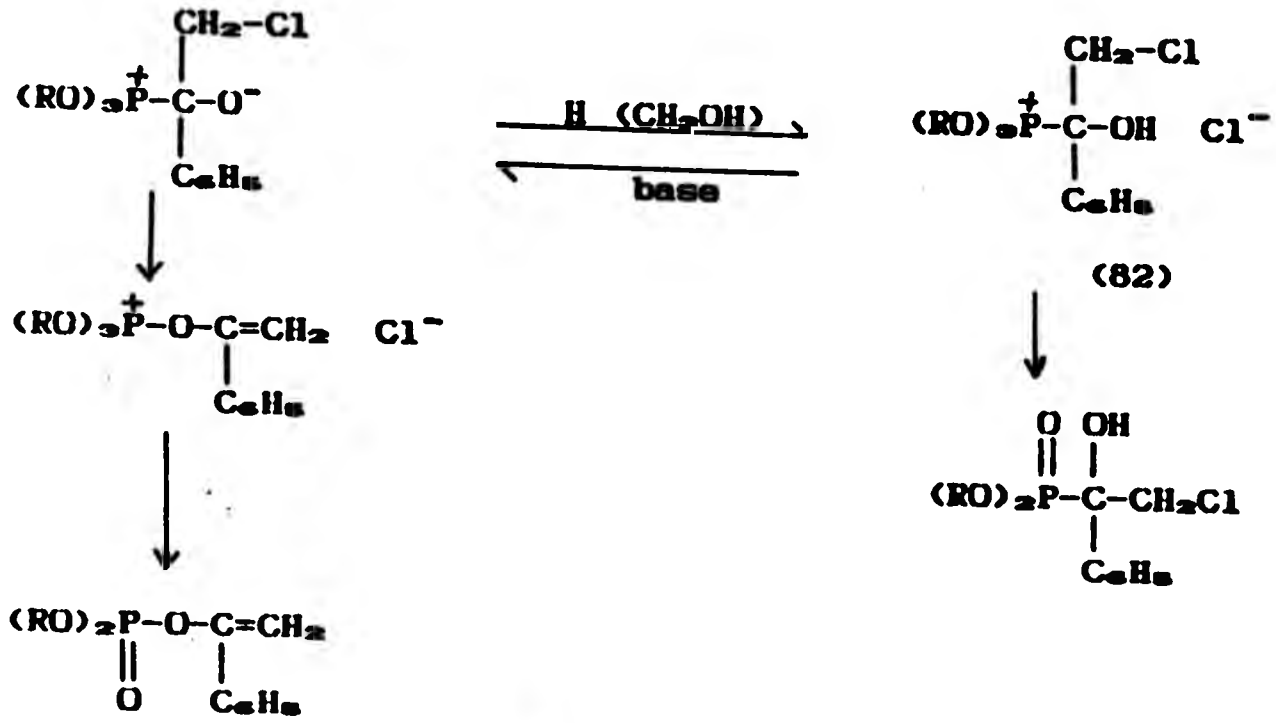
Table 1

Effect of varying the reactant ratio on the hydroxyphosphonate (HP), $(CH_3O)_2P(O)C(OH)(CH_2Cl)C_6H_4Y$, and vinyl phosphate (VP), $(CH_3O)_2P(O)OC(C_6H_4Y)=CH_2$, products concentration.

	$(CH_3O)_3P$: $ClCH_2COC_6H_4Y$ mole ratio			
	1 : 1	5 : 1	10 : 1	20 : 1
Y = H				
HP mole %	54.6	54.5	53.2	38.8
VP mole %	45.4	45.5	46.8	61.2
Y = Cl				
HP mole %	42.5	-	-	22.7
VP mole %	57.5	-	-	77.3

α-chloro-p-nitroacetophenone reaction (Table 1), with more vinyl phosphate being formed. A substantial increase in the amount of the side products, dimethyl phosphite, and dimethyl methylphosphonate was observed, on increasing the reactant ratio from 1:1 to 20:1, while a slight increase, 2 - 5 %, was obtained for trimethyl phosphate.

The possible explanation for the difference in the hydroxyphenacylphosphonate - vinyl phosphate product ratio could be that the excess of the trimethyl phosphite is acting as a base which reduces the concentration of the α-hydroxyphenacylphosphonium intermediate (82) (Scheme 30) and favours the vinyl phosphate formation. When the reaction of trimethyl phosphite with one mole equivalent of α-chloroacetophenone and pyridine was carried out, only the vinyl phosphate (80) and trimethyl phosphate were obtained. Pyridine being a strong base and a weak nucleophile readily abstracts the proton from the α-hydroxyphenacylphosphonium intermediate (82) (Scheme 30) causing the rapid rearrangement to vinyl phosphate through the vinyloxy phosphonium salt. The possibility of pyridine causing the rearrangement of formed α-hydroxyphosphonate was excluded, as no change was observed in authentic sample of the α-hydroxyphenacylphosphonate (81) with pyridine in methanol after six days.



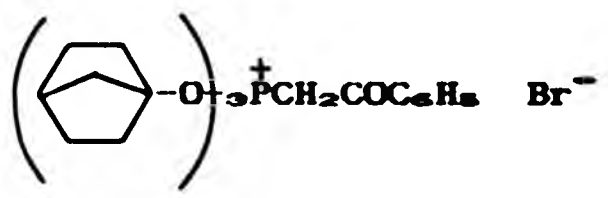
R = CH_3-

(Scheme 30)

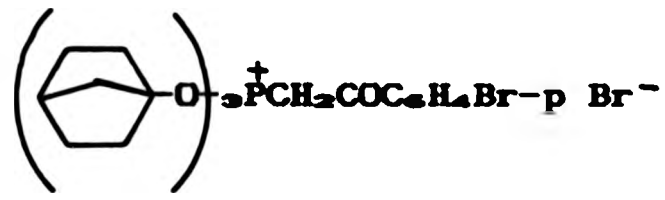
Reaction of trimethyl phosphite with α-chloro-p-nitroacetophenone was found to proceed much faster with the prefential formation of the corresponding vinyl phosphate (Table 12, page 150).

2.6 Isolation and decomposition of quasiphosphonium salts.

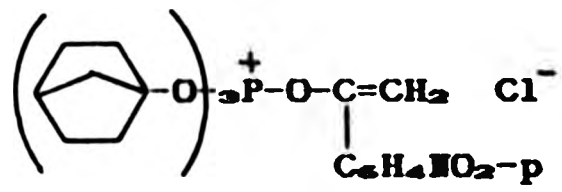
Stable quasiphosphonium salts obtained in solution in the reactions of trinorborn-1-yl phosphite in the present work were isolated by precipitation with anhydrous ether. The salts were highly stable so that they could be handled in the open air.



(57)



(66)



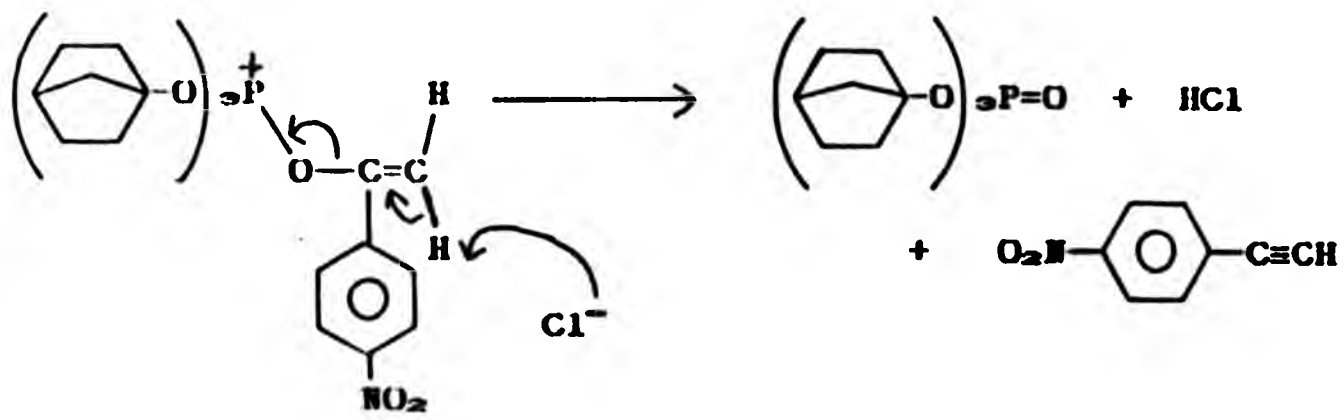
(63)

(75)

Decomposition of the phosphonium salts was carried out in deuterochloroform in sealed n.m.r. tubes and followed by ^1H and ^{31}P n.m.r. spectroscopy.

The phosphonium salts showed a high thermal stability. Decomposition of the phenacylphosphonium bromide (57) at 132 °C for 20 hours gave 67 % of undecomposed bromide, and decomposition at 148.5 °C for 6 hours, gave 33 % of the phosphonium bromide. The methylphosphonium iodide (75) was more resistant to decomposition than the phenacylphosphonium

bromide (57), about 71 % of undecomposed trinorbornyloxymethylphosphonium iodide (75) remaining after 24.6 hours of heating at 149 °C, and 41 % remaining after 154 hours. The vinyloxyphosphonium chloride (63) at 148 °C, underwent preferential cleavage of the vinyl oxygen bond to yield trinorborn-1-yl phosphate and p-nitrophenylacetylene by a bimolecular trans elimination reaction (Scheme 31). The products were confirmed by ^{31}P and ^{13}C n.m r. spectroscopy. This unusual cleavage of the Perkow intermediate results from the very high resistance of the norbornyl group to nucleophilic attack.

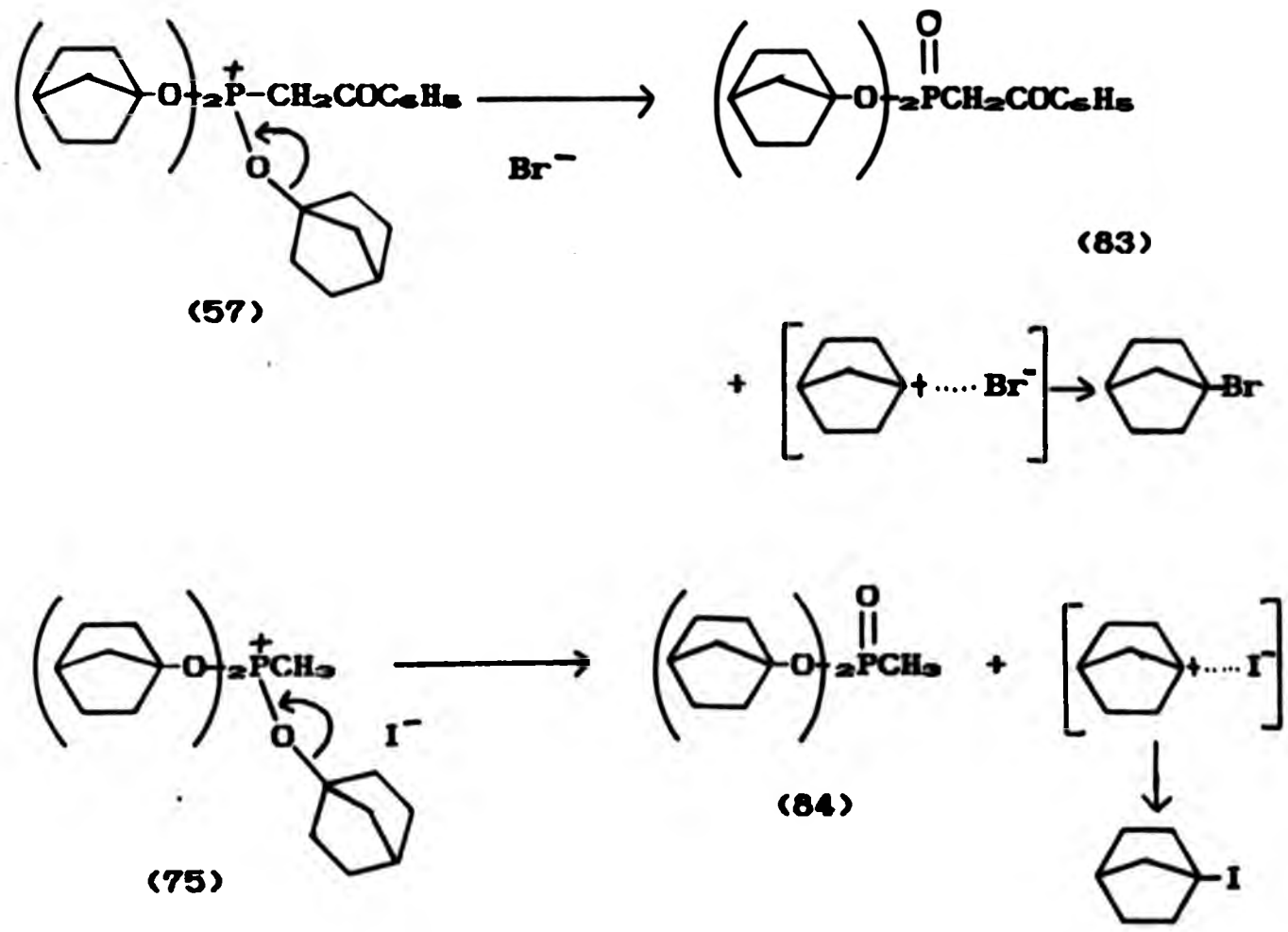


(63)

(Scheme 31)

The phenacylphosphonium bromide (57) yielded the expected Arbuzov product, dinorborn-1-yl phenacylphosphonate (83) δ_P 13.4, by an S_Ni cleavage (Scheme 32). Formation of side products was observed during the decomposition, as the ^{31}P n.m.r. spectrum of the solution after 6 hours of heating

at 148.5 °C, showed in addition to the phosphonium bromide (57) and the phenacylphosphonate (83), the presence of two unidentified compounds, δ_P 18.2 (d, J_{P-H} 8.9 Hz) and δ_P 12.3 (s). The presence of the unidentified compounds was not detected on complete decomposition. The methylphosphonium iodide (75) also gave the Arbuzov product, dinorborn-1-yl methylphosphonate (84) δ_P 24.6 (Scheme 32), with no other phosphorus-containing product detected during the course of decomposition.



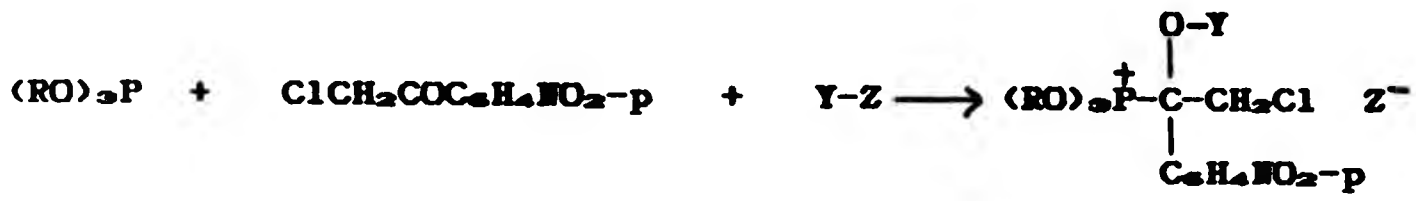
(Scheme 32)

2.7 Atempts to trap the betaine (75) in the reaction of trinorborn-1-yl phosphite and α-chloro-p-nitroacetophenone.

As postulated in the present investigation and by other authors, the Perkow reaction proceeds through nucleophilic attack of the carbonyl carbon to form a betaine (8) (Scheme 6, page 17), which then rearranges by migration of the phosphorus from carbon to oxygen to give the intermediate (Perkow) vinyloxyphosphonium salt and a subsequent dealkylation to the Perkow product. The betaine formation step has also being suggested by some authors as a possible first step in the Arbuzov reaction through rearrangement by intramolecular 1,2-shift of the phosphite group to the α-carbon to give the Arbuzov intermediate (Scheme 6, page 17). Though, in this investigation it was found that there was no common intermediate between the two reaction pathways, an attempt was made to trap the betaine and to investigate the conditions under which it might rearrange to both the Perkow and Arbuzov intermediates.

In the investigation, the reaction of trinorborn-1-yl phosphite with α-chloro-p-nitroacetophenone, which gives exclusively the vinyloxyphosphonium chloride (63) (Scheme 19), was used. Attempts were made to trap the betaine (67) (Scheme 20), by reaction with methanesulphonyl chloride, trifluoroacetic acid, methanol, benzoyl chloride and hydrogen chloride as shown below (Scheme 33). The reactions

were followed by ^1H and ^{31}P n.m.r. spectroscopy at room temperature.



(85 - 89)

	X	Z
(85): CH_3SO_2Cl	CH_3SO_2	Cl
(86): CF_3COOH	H	CF_3COO
(87): CH_3OH	H	CH_3O
(88): C_6H_5COCl	C_6H_5CO	Cl
(89): HCl	H	Cl

(Scheme 33)

In the presence of methanesulphonyl chloride, the betaine salt (85) was not observed, nor the vinyloxy-phosphonium chloride (63). The sulphonyl chloride was found to react with the phosphite to give trinorborn-1-yl phosphate as the major product and an unidentified compound, δ_P 49.7, which was assumed to be trinorborn-1-yloxy(methanethiyl)phosphonium chloride (90) based on the work of Gilbert,[87] Poshikus[88] and Hoffman[89] *et al.*, on the

reaction of triethyl phosphite with alkyl- and aryl-sulphonyl chlorides. The same products were obtained by a separate reaction of trinorborn-1-yl phosphite with methanesulphonyl chloride. The reaction probably proceeds in three consecutive stages as proposed by Poshikus *et al.*[90]

$$(RO)_3P + CH_3SO_2Cl \longrightarrow (RO)_3P{=}O + CH_3SOCl \quad (1)$$

$$(RO)_3P + CH_3SOCl \longrightarrow (RO)_3P{=}O + CH_3SCl \quad (2)$$

$$(RO)_3P + CH_3SCl \longrightarrow (RO)_3\overset{+}{P}SCH_3\ Cl^- \quad (3)$$

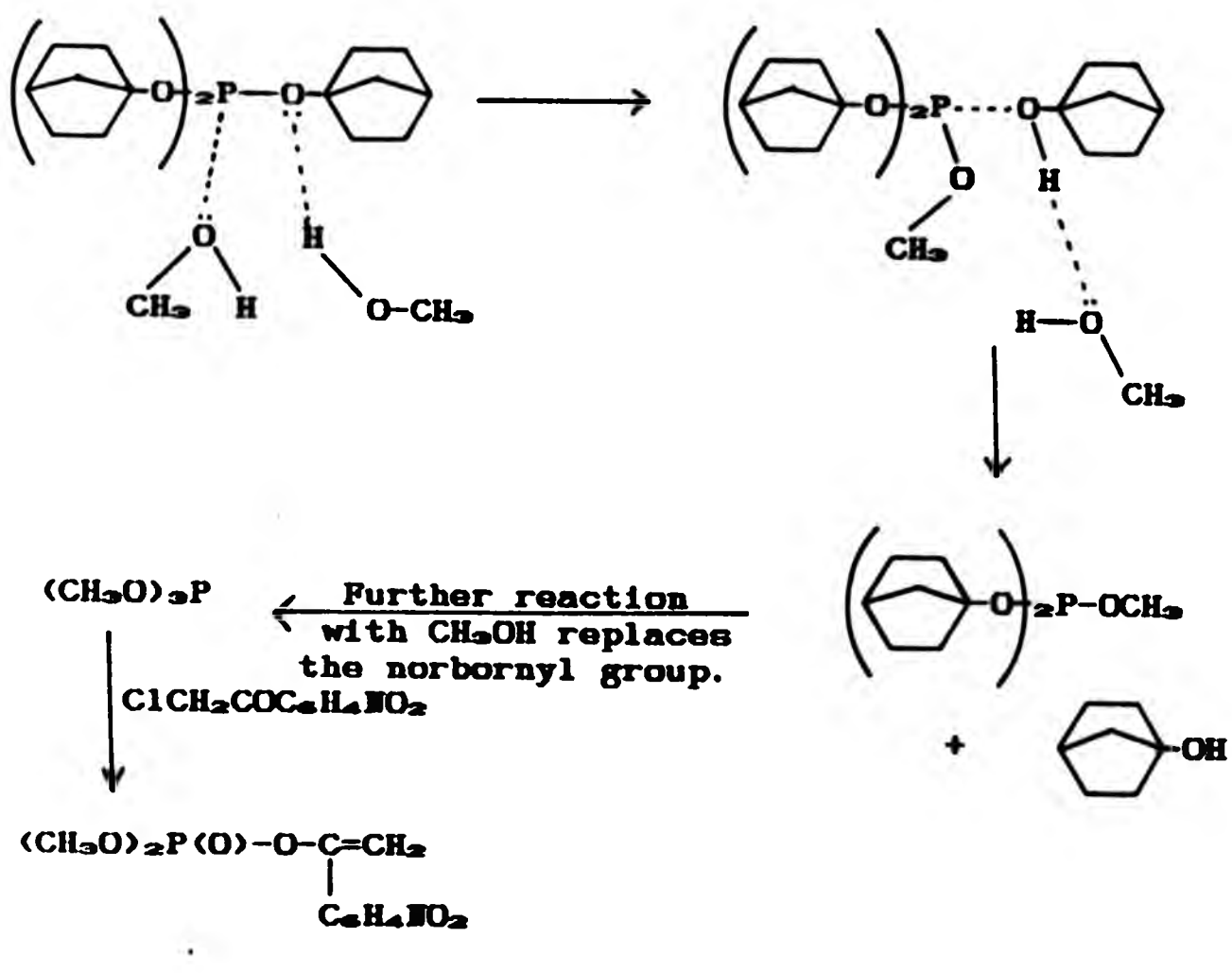
(90)

The first two steps involve reduction of the methanesulphonyl chloride to methanesulphenyl chloride which then in turn reacts with trinorborn-1-yl phosphite to yield the methanethiylphosphonium chloride (90). Dealkylation to the corresponding phosphonate occurs with simple alkyl groups but is not possible for norborn-1-yl under the experimental conditions used.

In the presence of trifluoroacetic acid, the vinyloxyphosphonium chloride (63), dinorborn-1-yl phosphite, and two unidentified compounds: (δ_P -12.7, and δ_P -14.2) were obtained. The betaine salt (86) was not obtained.

When the reaction of trinorborn-1-yl phosphite and α-chloro-p-nitroacetophenone was carried out in methanol, the presence of the betaine salt (87) was not detected in the mixture. Instead, an unidentified compound, δ_P -4.6, was obtained as the major product, together with

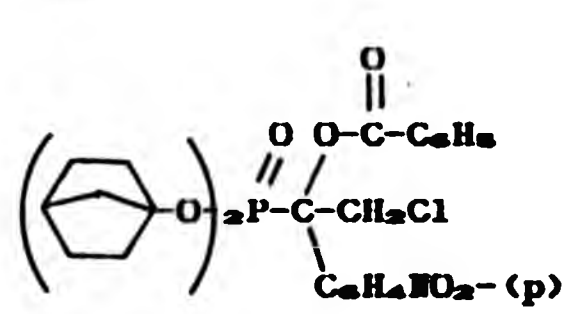
vinyloxyphosphonium chloride (63). The unidentified compound was assumed to be dimethyl 1-(p-nitrophenyl)vinyl phosphate (91) (authentic compound δ_P -4.8, Section 3.5, Table 12), formed by replacement of the norbornyl groups in trinorborn-1-yl phosphite by methoxy groups (Scheme 34) to form trimethyl phosphite which subsequently reacted with the acetophenone.



(Scheme 34)

The possibility of the norbornyloxy-methoxy group exchange occurring in the vinyloxyphosphonium chloride (63) was excluded by the ^{31}P n.m.r. spectrum of the vinyloxyphosphonium chloride (63) in methanol which showed no change after two months at room temperature.

Benzoyl chloride has been shown, (Section 2.4) to react very slowly with trinorborn-1-yl phosphite, whereas, the reaction of trinorborn-1-yl phosphite with α-chloro-p-nitroacetophenone is much faster (Section 2.2). The use of benzoyl chloride to trap the betaine as the α-benzoate derivative was therefore attempted. The reaction (Scheme 33) in the presence of benzoyl chloride gave the vinyloxyphosphonium chloride (63) as the major product, trinorborn-1-yl phosphate, and two unidentified compounds, δ_P 14.8 (*ca.* 9 %) and δ_P 30.8 (*ca.* 5 %). The unidentified compound at δ_P 30.8 is in the expected range for the α-benzoyloxyphosphonium chloride (88) while that at δ_P 14.8 is in the range for the α-benzoyloxyphosphonate (92), (based on analogy with trinorborn-1-yloxy(phenacyl)phosphonium chloride (57), δ_P 27.0, and dinorborn-1-yl phenacylphosphonate (83), δ_P 13.4.



(92)

The α-benzoyloxyphosphonate (92), could not however have been formed by dealkylation of the α-benzoyloxyphosphonium chloride (88) under the conditions used. Two unidentified compounds with similar ^{31}P chemical shift to those obtained above, were also observed in the reaction with hydrogen chloride discussed below.

In an attempt to trap the betaine by forming the α-hydroxyphosphonium chloride (89) in the presence of anhydrous hydrogen chloride, the effect of the hydrogen chloride on trinorborn-1-yl phosphite was investigated first by ^{31}P n.m.r. spectroscopy at various temperatures. It is known,[40] that the reaction of a trialkyl phosphite with hydrogen chloride goes through a phosphorus-protonated intermediate (93) leading to the dialkyl phosphite (equation

$$(RO)_3P + HCl \rightleftharpoons (RO)_3\overset{+}{P}H\ Cl^- \longrightarrow (RO)_2P(O)H + RCl \quad \ldots (1)$$

(93)

1), the first stage of the reaction being reversible. With a sterically hindered alkyl group for which dealkylation does not occur readily, the equilibrium is shifted towards the phosphorus-protonated form at low temperature.

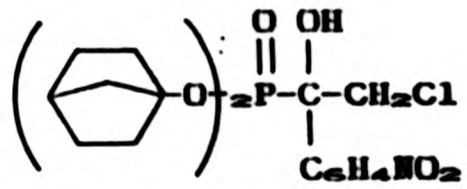
^{31}P n.m.r. of trinorborn-1-yl phosphite in deuterochloroform saturated with anhydrous hydrogen chloride (2 mole equivalent) was carried out at 27°, 0°, 20°, -40° and -55 °C (n.m.r. spectrometer temperature). The spectrum at 27 °C gave a broad signal at δ_P 14.8 which was assumed to

be the protonated trinorborn-1-yl phosphite (93) (equation 1, R = $C_7H_{11}O$-), with the equilibrium lying virtually completely to the protonated form as no change in the chemical shift was observed on lowering the temperature to -55 °C. An attempt to recover the trinorborn-1-yl phosphite from the protonated phosphite solution by pumping off the hydrogen chloride and solvent in *vacuo* for 10 hours resulted in a mixture, in which the ^{31}P n.m.r. at -55 °C showed the presence of trinorborn-1-yl phosphite (δ_P 142.2), protonated trinorborn-1-yl phosphite (δ_P 19.7, $^1J_{P-H}$ 829.9 Hz), dinorborn-1-yl phosphite (δ_P 1.03, $^1J_{P-H}$= 687.1 Hz) and trinorborn-1-yl phosphate (δ_P -10.42). Dinorborn-1-yl phosphite was formed probably by the hydrolyses of the protonated trinorborn-1-yl phosphite by atmosperic moisture, and trinorborn-1-yl phosphate formed by aerial oxidation.

Addition of α-chloro-p-nitroacetophenone to protonated phosphite (93) solution at room temperature gave no reaction after 20 hours. ^{31}P n.m.r. of the solution showed only the presence of the protonated phosphite (93) (δ_P 14.5) plus a small amount (7 %) of dinorborn-1-yl phosphite. ^{31}P n.m.r. of the mixture run at -55 °C after two weeks at room temperature showed the presence of vinyloxyphosphonium chloride (63), trinorborn-1-phosphate and two unidentified compounds, δ_P 16.6 (*ca.* 7 mol %) and δ_P 32.1 (*ca.* 3 mol %).

The unidentified compounds at δ_P 32.1, and δ_P 16.6 are in the expected range for the α-hydroxyphosphonium chloride (89), and α-hydroxyphosphonate (94) respectively, based on

the known chemical shifts for trinorborn-1-yloxy(phenacyl)-phosphonium chloride (57), δ_P 27.0, and dinorborn-1-yl phenacylphosphonate (83), δ_P 13.4, although the latter, is unlikely to be formed under the experimental conditions, by a process involving dealkylation of the phosphonium salt.



(94)

2.8 The effect of silver perchlorate in the reaction of trimethyl phosphite and iodoacetone.

Chopard *et al.*,[10] reported the detection of a ketophosphonium perchlorate (95) (Arbuzov intermediate), identified only by infra-red spectroscopy, from the reactions of chloro- and iodo-acetone with trimethyl phosphite in solution of benzene, in the presence of silver perchlorate (Scheme 35). The usual Perkow reaction with chloroacetone did not occur. Addition of quinoline was then said to give the Arbuzov product, although this was not isolated. The effect of the silver ion on the course of reaction of trimethyl phosphite with iodoacetone was therefore reinvestigated by carrying out the reaction in an n.m.r. tube and was followed by ^{31}P n.m.r. spectroscopy.

$$CH_3COCH_2X + (CH_3O)_3P + AgClO_4$$

$$\downarrow$$

$$(CH_3O)_3\overset{+}{P}CH_2COCH_3\ ClO_4^- + AgI$$

(95)

$$\downarrow C_9H_7N$$

$$(CH_3O)_2P(O)CH_2COCH_3 + C_9H_7\overset{+}{N}CH_3\ ClO_4^-$$

(Scheme 35)

The present studies showed no signal assignable to a ketophosphonium ion (δ_P ca. 40) or a ketophosphonate (δ_P ca. 20) at any stage. Two phosphorus containing compounds: trimethyl phosphate (δ_P 1.8) formed by partial oxidation of the trimethyl phosphite, and tetramethyl pyrophosphate (96), $[(CH_3O)_2P(O)O]_2$, (δ_P -10.4) were obtained, together with acetone.

The effect of silver ion on trimethyl phosphite alone was to move the chemical shift upfield from δ_P 140 to 127 by virtue of reversible complex formation, δ_P 127 being the chemical shift for the undissociated complex (97) in the absence of excess trimethyl phosphite.[42,43] Additional

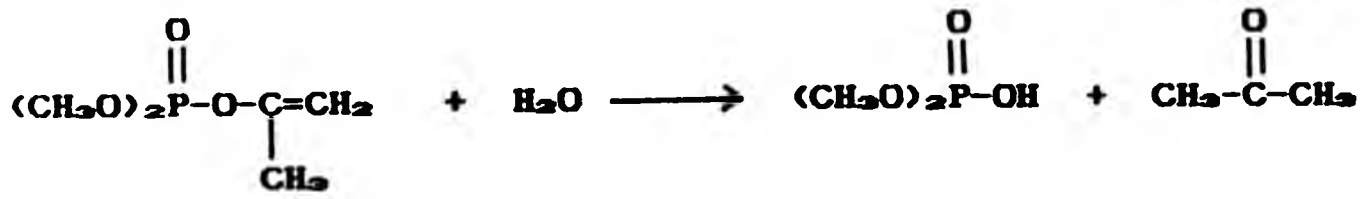
$$4(CH_3O)_3P + AgClO_4 \rightleftharpoons Ag[(CH_3O)_3P]_4^+ ClO_4^-$$

(97)

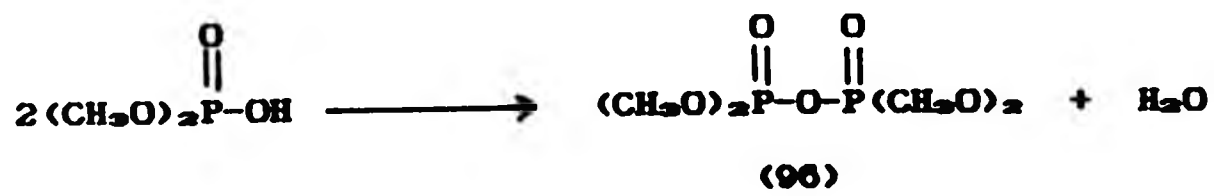
intermediate resonating at δ_P 36 was observed in the mixture which is probably due to the slight dissociation of the complex (97) into another reversible species, though the chemical shift is in the region observed for dimethyl methylphosphonate an isomeric product of trimethyl phosphite as ^{31}P n.m.r. of an authentic sample of dimethyl methylphosphonate in the presence of silver perchlorate was found to shift downfield from δ_P 30.9 to 35.1. Addition of iodoacetone to the trimethyl phosphite-silver perchlorate mixture, gave an immediate precipitation of silver iodide with the formation of trimethyl phosphate and tetramethyl

pyrophosphate. No change in the spectrum was observed on adding quinoline to the mixture as would be expected from the results of Chopard *et al.*[10] The previously obtained intermediate at δ_P 36 was found to increase slightly on adding iodoacetone but disappeared after about 20 minutes of the reaction time. ^1H n.m.r. of the reaction mixture showed in addition to the presence of the methyl groups in trimethyl phosphate and the pyrophosphate (96) (δ_H 3.3 - 3.8), a large signal at δ_H 1.6 which was assumed to be acetone [authentic sample δ_H (C_6D_6) 1.6], and a signal at δ_H 3.22 due to methyl perchlorate [authentic sample δ_H (C_6D_6) 3.1, lit.[44] δ_H (CCl_4) 4.22].

Formation of the tetramethyl pyrophosphate, due to the presence of moisture possibly reacting with the expected product, dimethyl 1-methylvinyl phosphate (98), (Scheme 36) was excluded as several repetitions of the procedure under



(98)



(96)

(Scheme 36)

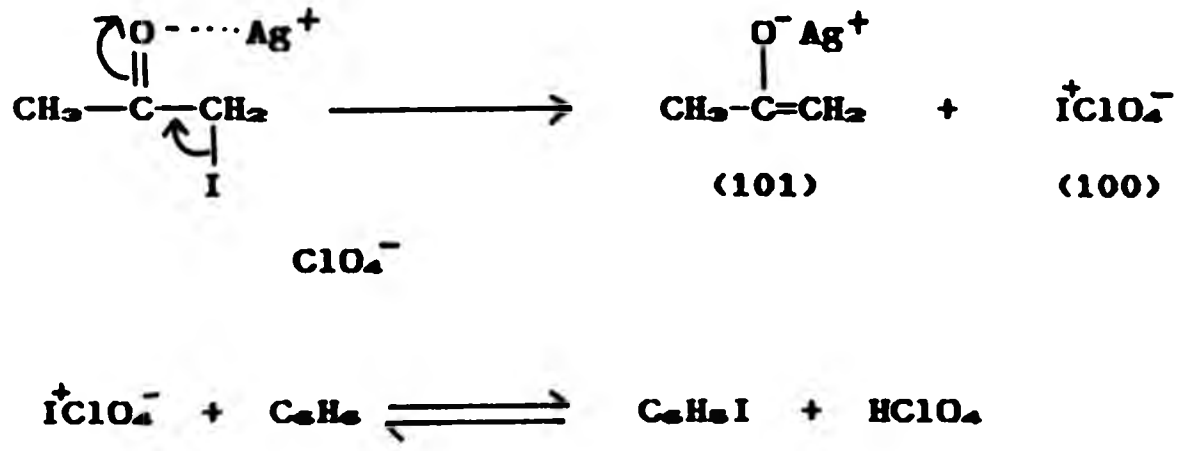
improved anhydrous conditions (see Table 15 page 177), still gave trimethyl phosphate and the pyrophosphate (96) as the only phosphorus containing products. The presence of moisture in silver perchlorate was found to hydrolyse the trimethyl phosphite to dimethyl phosphite (δ_P 14.8, $^1J_{H-P}$ 732.4 Hz) immediately on mixing. Authentic samples of dimethyl 1-methylvinyl phosphate (98) and dimethyl acetonylphosphonate (99), the expected reaction products in the absence of silver perchlorate showed changes in the ^{31}P chemical shift from δ_P -4.8 to -5.1 and δ_P 21.8 to 25.5 respectively with no other product detected after 24 hours of mixing. The formation of these products in the reaction with silver perchlorate present, can therefore be excluded.

In order to ascertain the course of the reaction through which the pyrophosphate (96) and acetone were formed, the effect of silver perchlorate on iodoacetone was investigated by ^1H n.m.r. The ^1H n.m.r. spectrum of the reaction mixture of iodoacetone and silver perchlorate in benzene-d_6 showed the presence of signals at δ_H 2.86 and δ_H 4.86 (with integration ratio 3:2) which were assigned to the group CH_3COCH_2. A complex mixture was assumed to be formed, as the expected yellowish precipitate of silver iodide (Equation 1) was not obtained (see experimental, page 181).

$$CH_3COCH_2I + AgClO_4 \not\longrightarrow CH_3COCH_2^+ \; ClO_4^- + AgI \quad \ldots(1)$$

An immediate precipitation of silver iodide was however observed when trimethyl phosphite was added to the iodoacetone-silver perchlorate mixture, with the resultant formation of trimethyl phosphate, tetramethyl pyrophosphate, and acetone.

A likely reaction occurring between iodoacetone and silver perchlorate is the formation of iodonium perchlorate (100) and the acetonyl salt (101), through the silver ion assisted elimination of iodonium ion (Scheme 37), the iodonium perchlorate subsequently reacting with benzene

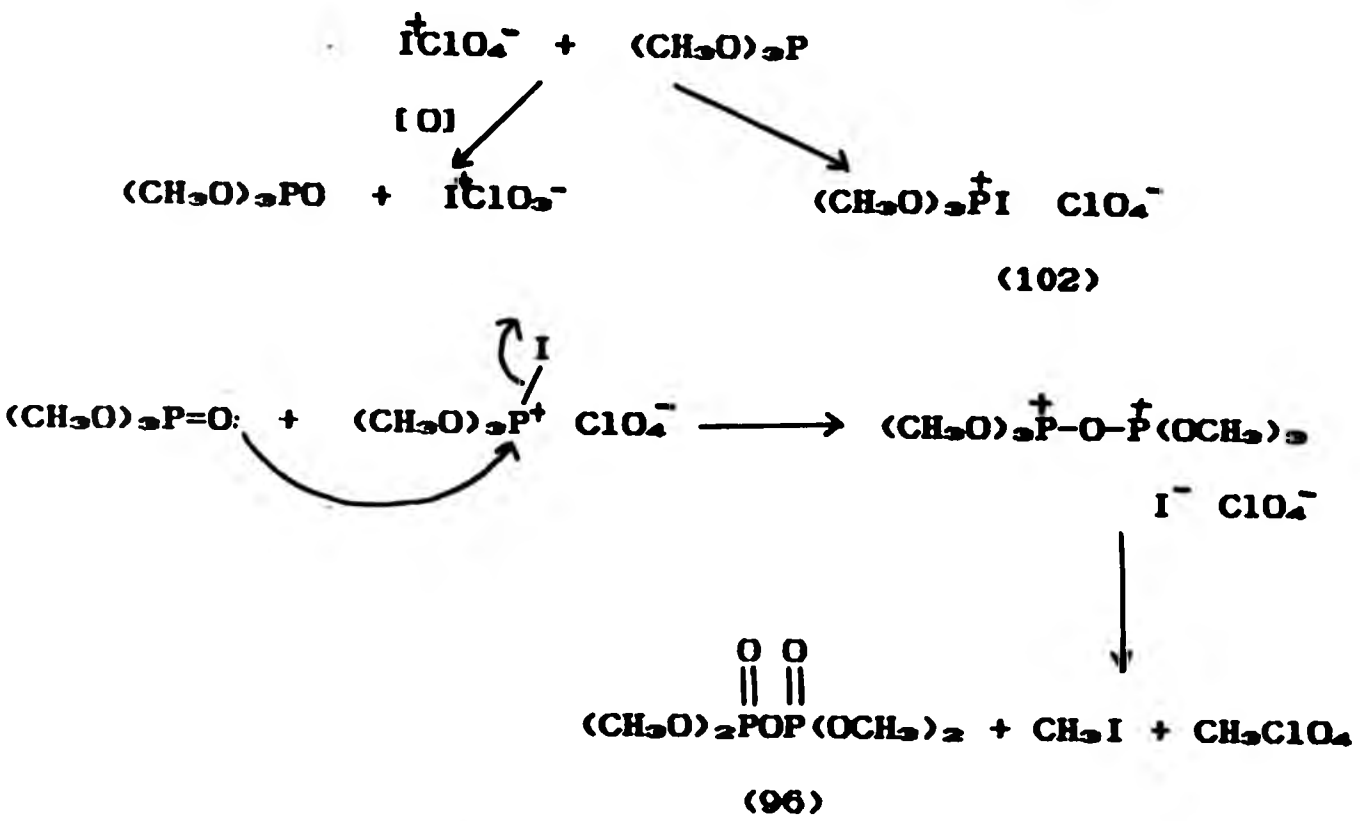


(Scheme 37)

to form iodobenzene and perchloric acid, a method used in preparing iodoaromatic compounds.[48] The observed signals at δ_H 7.9 and 7.2 in the reaction product, (see experimental, page 181) were assumed to be due to perchloric acid and iodobenzene respectively. The anhydrous perchloric acid, a violent oxidising agent towards organic compounds,[48] slowly decomposes the acetonyl salt (101) and iodobenzene formed as

observed in the reaction mixture after 20 hours of reaction time.

Reaction of trimethyl phosphite with iodoacetone in the presence of silver perchlorate may therefore involve a number of concomitant reaction stages interwoven with each other. From the experimental results obtained (see Table 15 page 177), some unreacted trimethyl phosphite-silver perchlorate complex was present in the reaction mixture after 24 hours, and the presence of unreacted iodoacetone was also usually observed. The complex formed between trimethyl phosphite and silver perchlorate has been shown to be a 4:1 complex,[42,43] which implies that, according to the Chopard'[10] procedure adopted in the present investigation, the silver perchlorate used was in large excess (see Table page 15). The excess silver perchlorate probably reacted with the iodoacetone to give the acetonyl salt (101) and iodonium perchlorate (100) (Scheme 37). The iodonium perchlorate could then undergo a further reaction with trimethyl phosphite to give both the trimethyl phosphate, by oxidation, and trimethyloxyiodophosphonium perchlorate (102) (Scheme 37). Interaction of the trimethyloxyiodophosphonium perchlorate and trimethyl phosphate would then give tetramethyl pyrophosphate (Scheme 38).

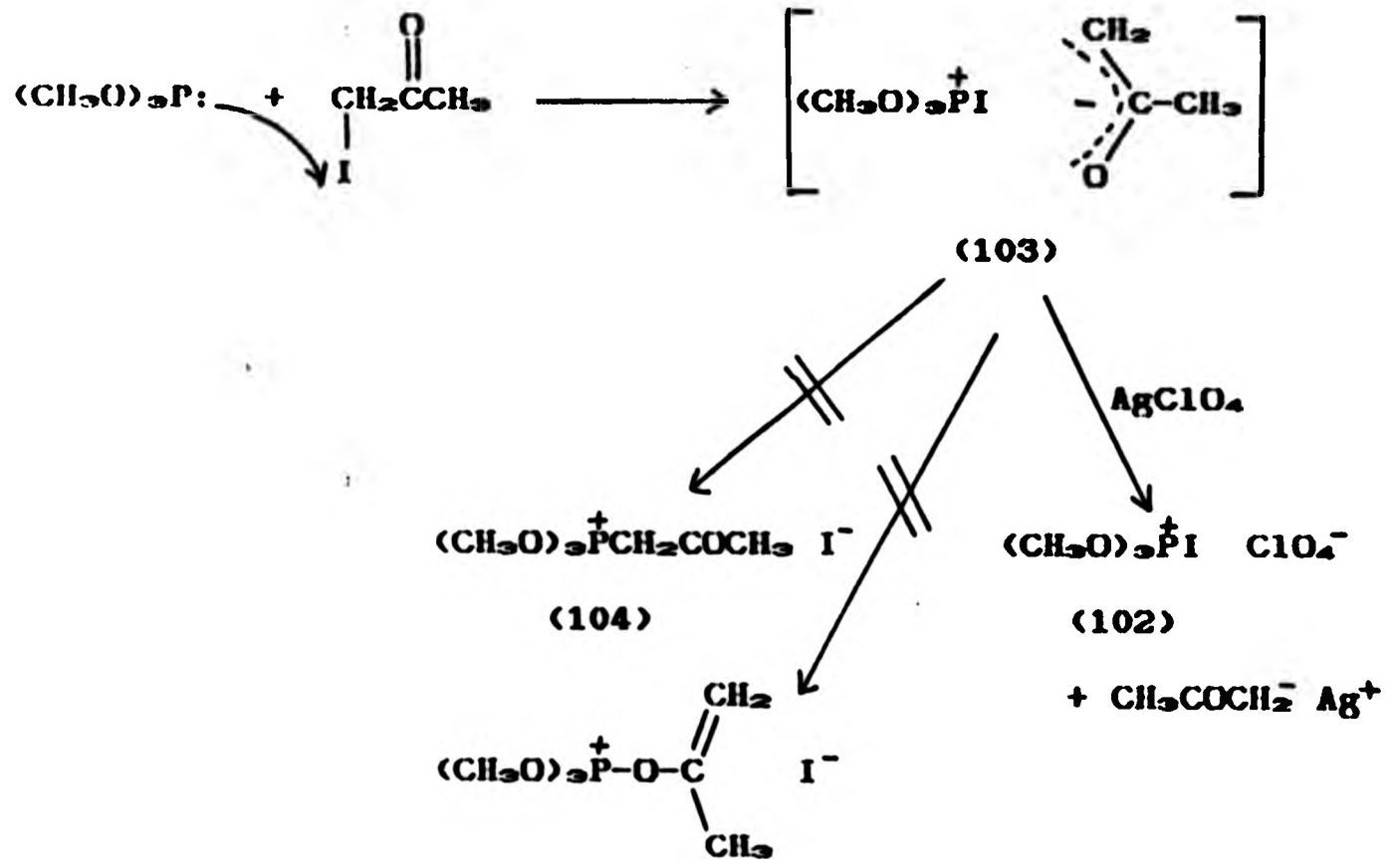


(Scheme 38)

Methyl iodide was not observed as this would quickly form silver iodide with silver ion in the reaction mixture.

Another possible route to the formation of trimethyloxyiodophosphonium perchlorate (102) is through nucleophilic attack of the trimethyl phosphite on positive iodine in iodoacetone (Scheme 39), to give the ion-pair (103), which then reacts with silver perchlorate to afford the iodophosphonium perchlorate (102). This route will be feasible if the iodophosphonium perchlorate (102) is more stable than the alternate Arbuzov intermediate, trimethyloxy(acetonyl)phosphonium iodide (104).

Trimethyl phosphate could also be formed by oxidation with perchloric acid (Equation 2), which is formed *in situ*



(Scheme 39)

by the interaction of iodonium perchlorate with solvent benzene (Scheme 37).

$$(CH_3O)_3P + HClO_4 \longrightarrow (CH_3O)_3PO + HClO_3 \quad ...(2)$$

The acetonyl salt (101) (Scheme 37), could react with either the chloric acid, formed from trimethyl phosphite oxidation (Equation 2), to give acetone and silver chlorate, or with perchloric acid to afford silver perchlorate and acetone (Equation 3 and 4).

$$CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2^- Ag^+ + HClO_3 \longrightarrow CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 + AgClO_3 \quad ...(3)$$

$$CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2^- Ag^+ + HClO_4 \longrightarrow CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 + AgClO_4 \quad ...(4)$$

2.9 Structural analysis by spectroscopy and X-ray crystallograpy

2.9.1 Nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance spectroscopy, in particular ^{31}P n.m.r. served as a useful tool for studying the reaction pathways in the present investigation and characterization of the various products obtained. ^{31}P n.m.r. chemical shifts depend strongly on the nature of the atoms directly bonded to the phosphorus, and the kind of bond involved, with substitution at some distance from the phosphorus atom having relatively small effect.[47]

^{31}P n.m.r. chemical shifts of the various compounds obtained in the present investigation are shown in Table 2. Compounds derived from phosphorus(III) esters of neopentyl- [$(CH_3)_3CCH_2$-], 2,2-diethylbutyl- [$(CH_3CH_2)_2CCH_2$-] and 2,2,2-triphenylethyl- [$(C_6H_5)_3CCH_2$-] alcohol all have chemical shifts in the expected ranges as previously obtained for quasiphosphonium salts, phosphonates, and phosphates[1,2,12] with negligible effect from the bulkyl γ-substituent. However a large upfield shift (*ca.* 10 - 15 ppm), with respect to the previously obtained analogues, and those in the present investigation, was obtained for the quasiphosphonium salts, the Arbuzov cleavage products, and trinorborn-1-yl phosphate derived from trinorborn-1-yl phosphite. A slight downfield shift (*ca.* 1 - 2 ppm) was

obtained for trinorborn-1-yl phosphite compared to the other trialkyl phosphites.

Table 2

^{31}P n.m.r. chemical shifts for phosphorus(III) esters, corresponding quasiphosphonium salts, phosphates, and phosphonates obtained in the present investigation.

COMPOUND	δ_P	J / Hz
R = $(CH_3)_3CCH_2-$		
$(RO)_2P(O)CH_2COCH_3$	19.4	
$(RO)_2P(O)OC(CH_3):CH_2$	-6.8	
$(RO)_3\overset{+}{P}-CH_2COC_6H_4Br-p\ Br^-$	39.8	
$(RO)_2P(O)CH_2COC_6H_4Br-p$	18.9	
$(RO)_2P(O).O.C(C_6H_4Br-p):CH_2$	-6.2	
R = $(C_2H_5)_3CCH_2-$		
$(RO)_3P$	139.7	
$(RO)_2P(O)H$	8.2	$^1J_{P-H}$ 691
$(RO)_3P{\cdot}O$	-0.6	
$(RO)_3\overset{+}{P}CH_2COC_6H_5\ Br^-$	40.6	
$(RO)_2P(O)CH_2COC_6H_5$	19.7	
$(RO)_2P(O)OC(C_6H_5):CH_2$	-6.0	

Table 2 continued

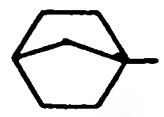
Compound	δ_P ppm	J / Hz
R = 		
$(RO)_3P$	141.4	
$(RO)_2P(O)H$	-0.4	$^1J_{P-H}$ 685.3
$(RO)_3P$ O	-10.2	
$(RO)_3\overset{+}{P}CH_2COC_6H_5$ Br^-	26.7	
$(RO)_3\overset{+}{P}CH_2COC_6H_5$ Cl^-	26.8	$^2J_{P-H}$ 18.0
$(RO)_3\overset{+}{P}CH_2COC_6H_4Br$-p Br^-	26.3	$^2J_{P-H}$ 18.0
$(RO)_3\overset{+}{P}CH_2COC_6H_4NO_2$-p Br^-	25.2	$^2J_{P-H}$ 17.2
$(RO)_3\overset{+}{P}OC(C_6H_4NO_2$-p$):CH_2$ Br^-	-16.9	
$(RO)_3\overset{+}{P}OC(C_6H_4NO_2$-p$):CH_2$ Cl^-	-17.1	
$(RO)_3\overset{+}{P}OC(CH_3):CH_2$ Cl^-	-16.9	
$(RO)_3\overset{+}{P}CH_2COCH_3$ Cl^-	26.4	$^2J_{P-H}$ 18.5
$(RO)_3\overset{+}{P}CH_3$ I^-	36.9	$^2J_{P-H}$ 16.4
$(RO)_2P(O)CH_3$	24.4	$^2J_{P-H}$ 17.6
$(RO)_2P(O)CH_2COC_6H_5$	13.4	$^2J_{P-H}$ 23.1
$(RO)_2P(O)CH_2COC_6H_4NO_2$-p	12.2	

Table 2 continued

Compound	δ_P [a]	J / Hz
R = $(C_6H_5)_3CCH_2-$		
$(RO)_3P$	138.7	
$(RO)PCl_2$	177.1	
$(RO)_2P(O)H$	6.7	$^1J_{P-H}$ 717.5
$ROP(C_6H_5)_2$	116.1	
$ROP(O)(C_6H_5)_2$	32.9	
$ROP^+(C_6H_5)_2CH_3\ I^-$	72.7	

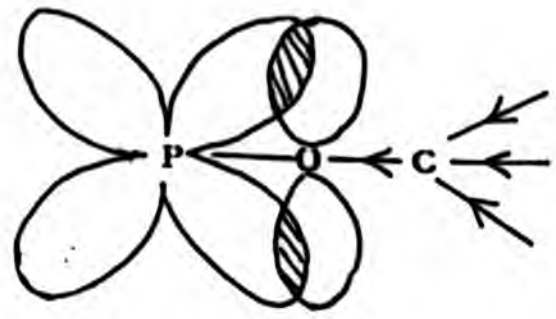
a Relative to 85 % H_3PO_4 as external standard; up-field positive. Solvent: $CDCl_3$

Several authors[48] have attempted to develop a unified theoretical foundation for ^{31}P chemical shifts of phosphorus compounds. Using approximate quantum mechanical calculations, Letcher and Van Wazer[49] demonstrated that three factors appear to dominate ^{31}P chemical shift differences ($\Delta\delta$):

$$\Delta\delta = -C\ \Delta X\pi + k\ \Delta n\pi + A\ \Delta\theta$$

where ΔX is the difference in electronegativity of X in the P-X bond, $\Delta n\pi$ is the change in the π-electron overlap between the P-X bond, $\Delta\theta$ is the change in the σ-bond angle, and C, k and A are constants.

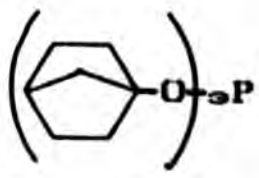
The π-electron overlap effect, which will be affected by the nature of the alkyl group, can probably be eliminated in accounting for the increased shielding observed for the



dπ - pπ electron overlap in the phosphorus-oxygen bond.

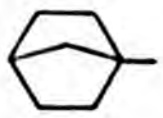
norbornyl compounds because there is no significant change in the chemical shift of the trialkyl phosphites (Table 3), in passing through the various alkyl derivatives to the norbornyl phosphite.

Table 3

	δ_P
$(CH_3O)_3P$	139.7
$[(CH_3)_3CCH_2O]_3P$	138.4
$[(CH_3CH_2)_3CCH_2O]_3P$	139.7
$[(CH_3)_3CO]_3P$	138.1 [49]
	141.4

Tri-t-butyl phosphate, $[(CH_3)_3CO]_3PO$, and di-t-butyl phosphite, $[(CH_3)_3CO]_2P(O)H$, have been shown,[80] to have high upfield shifts (with respect to 85 % H_3PO_4) which are similar to those observed in the present investigation for trinorbornyl derivatives (Table 4). The increased shielding observed in the t-butyl derivatives was attributed to the electron releasing methyl substituents increasing the electron density on the phosphorus *via* the linking oxygen.[80] This high electron density around phosphorus is thus partly responsible for the enhanced nucleophilicity of tri-t-butyl phosphite. However, this cannot be the case with norbornyl derivatives since there is no comparable electronic effect in the norbornyl group. This is demonstrated by the lack of reaction of the trinorborn-1-yl phosphite with either α-chloroacetone or phenacyl chloride at room temperature, due to its weak nucleophilicity.

Table 4

	δ_P (ppm)	
R	$(RO)_3P$ O	$(RO)_2P(O)H$
$(CH_3)_3CCH_2$-	-1.1	8.2
	-10.2	-0.3
$(CH_3)_3C$-	-13.3	-3.8

An increase in shielding caused probably by a change in the σ-bond angle at phosphorus due to steric crowding was investigated by carrying out the X-ray structural analysis of the Arbuzov intermediate, trinorborn-1-yloxy(phenacyl)-phosphonium bromide (57) and the Perkow intermediate, trinorborn-1-yloxy-1-(p-nitrophenyl)vinyloxyphosphonium chloride (63) (see page 102). From the X-ray analysis of the phosphonium salts, a distortion of the configuration around phosphorus, from the ideal *Td* tetrahedral symmetry was observed, due probably to steric effects as would be expected when all four groups attached to phosphorus are not identical. However, due to lack of X-ray analysis information on any other trialkyloxyphosphonium salt, the degree of distortion observed especially in the phosphonium bromide (65) cannot be correlated with the increase in shielding obtained compared to the neopentyloxy or other trialkyloxy analogue.

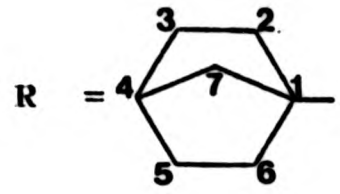
^{13}C n.m.r. spectroscopy was also found to be useful in characterization of the various trinorbornyl phosphite derivatives obtained (Table 5). The norbornyl α-carbon showed marked variation in chemical shift with different substituents on the phosphorus atom, with reference to trinorbornyl phosphite. The variation is probably due to the inductive effect of the substituents at the norbornyl α-carbon.

Table 5

^{13}C n.m.r. parameters[a] of compounds derived from trinorborn-1-yl phosphite

Compound No.	C1	C2,6	C3,5	C4	C7	C8	C9	C10	C11,11'	C12,12'	C13
40	86.1 (6.1)	35.1 (6.7)	30.0	33.6	43.0 (7.9)						
41	89.2 (7.3)	33.6 (7.9)	29.8	33.6	42.1 (4.9)						
57	97.9 (12.2)	33.8 (3.0)	29.6	32.8	42.4 (3.7)	40.6 (135)	190.2 (7.9)	135.7 (7.3)	130.1	129.0	134.6
66	98.0 (12.2)	33.8 (3.0)	29.6	32.8	42.4 (3.7)	40.7 (136)		134.3 (8.5)	131.8	132.4	130.3
63	100.5 (11.6)	33.3 (3.0)	29.5	32.7	42.3 (4.3)	150.4 (9.8)	105.4	137.5 (7.9)	127.0	124.4	148.8
75	97.3 (11.0)	34.1 (3.0)	29.8	33.0	42.8 (3.7)	16.1 (130)					
83	89.9 (7.9)	34.0 (2.4)	29.7	33.3	42.2 (4.3)	41.5 (130)	192.4 7.3	137.1 (7.3)	129.3	128.5	133.3
84	97.4 (11.0)	34.0 (3.0)	29.8	32.8	42.8 (4.3)	15.4 (130)					

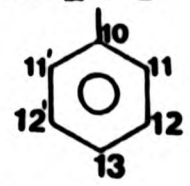
[a] Chemical shift (in ppm) relative to TMS; up field positive. J_{P-C} / Hz in parentheses.



$(RO)_3P$ $(RO)_3P \cdot O$

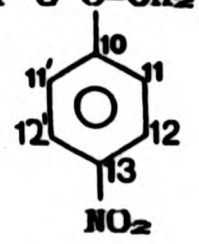
(40) (41)

$(RO)_3\overset{+}{P}\overset{8}{C}H_2\overset{9}{C}=O \quad Br^-$



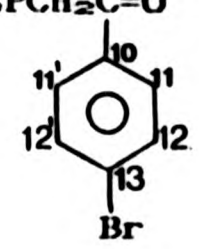
(57)

$(RO)_3\overset{+}{P}-O-\overset{8}{C}=\overset{9}{C}H_2 \quad Cl^-$



(63)

$(RO)_3\overset{+}{P}\overset{8}{C}H_2\overset{9}{C}=O \quad Br^-$



(66)

$(RO)_3\overset{+}{P}\overset{8}{C}H_3 \quad I^-$

(75)

$(RO)_2P(O)\overset{8}{C}H_2\overset{9}{C}=O$

(83)

$(RO)_2P(O)\overset{8}{C}H_3$

(84)

^{1}H n.m.r. spectroscopy was used in studying reaction pathways, and in studying decomposition of quasiphosphonium salts. It was also used in characterization of the various compounds prepared.

The 80 MHz ^{1}H n.m.r. spectrum of 2,2-diethylbutan-1-ol (26) (Fig 1) was found to show a second order effect with the 1:3:3:1 structure of the methylene band not easily recognised and the 1:2:1 structure of the methyl band displaying a high roofing effect. The spectrum at 200 MHz (Fig 1) displays some roofing effect indicative of second order in a near first order spectrum, with the 1:3:3:1 structure of the methylene band and the 1:2:1 structure of the methyl band easily recognised. On a straight forward first order basis, the chemical shift obtained from the spectrum (200 MHz) was δ 0.79 for the CH_3 group and δ 1.24 for the CH_2 group, with an estimated spin coupling constant of 7.3 Hz and $\Delta\delta/J$ value of 11. The first order rule of (n+1) can still be applied.

Spin simulations, A_3B_2, for the alcohol at different spectrometer frequencies are shown in Figure 2, and spin simulation at 200 MHz with very small line width and resolution enhancement is shown in Figure 3. For a given spin system of the AnBm type, the appearance of the spectrum depends on three parameter: V_A, V_B and J_{AB}.[82,83] The intensities in the spectrum depend only on the magnitude of $J_{AB}/(V_A-V_B)$ and the whole spectrum may be characterized in terms of this single parameter. The AnBm spectrum can be

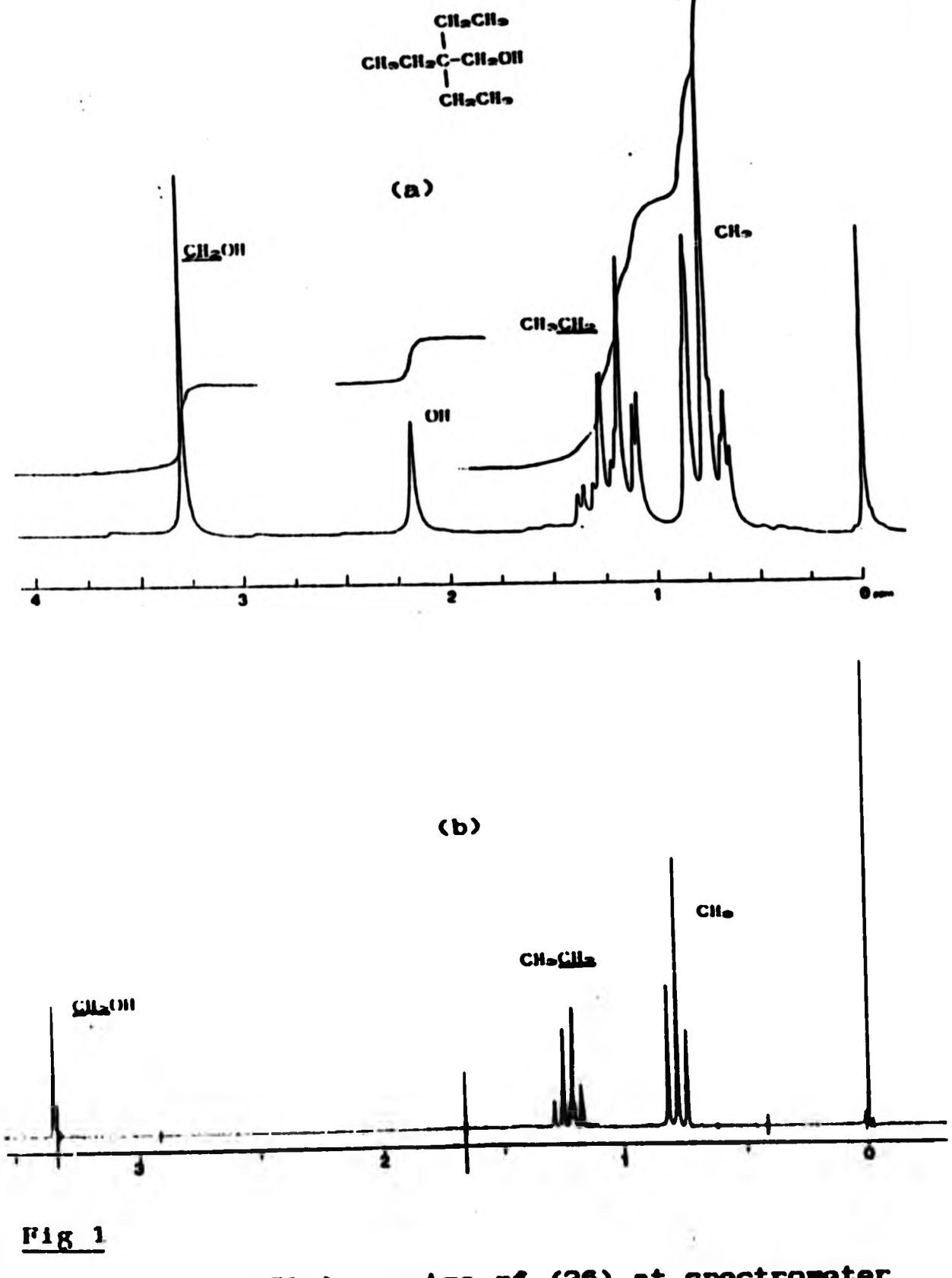


Fig 1

^1H n.m.r. ($CDCl_3$) spectra of (26) at spectrometer frequencies: (a) 80 MHz, and (b) 200 MHz.

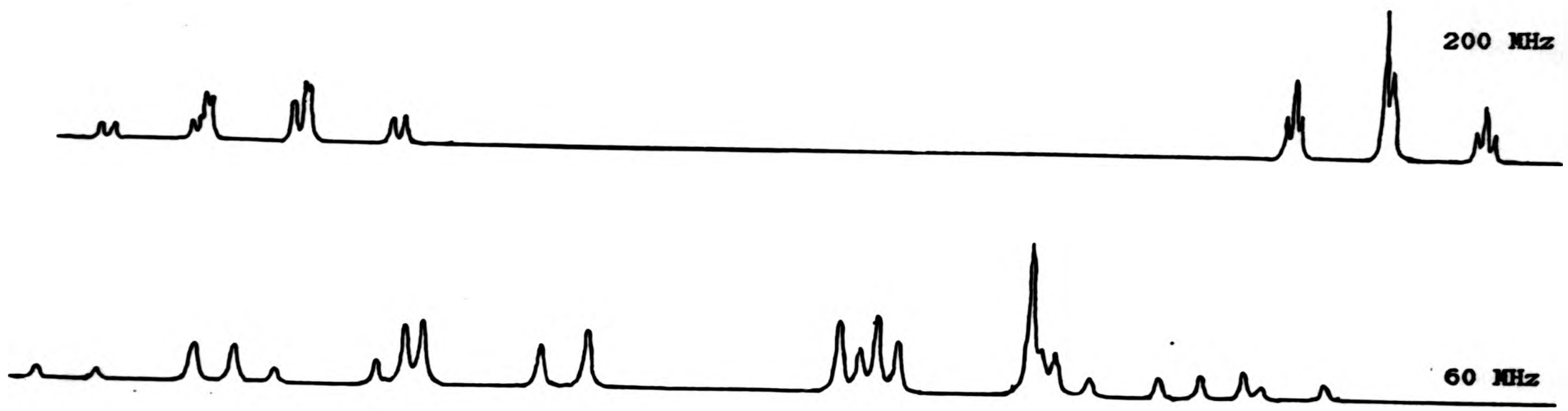


Fig 2

A_3B_2 spin simulation on $(CH_3CH_2)_3CCH_2OH$ (26)

at different spectrometer frequencies.

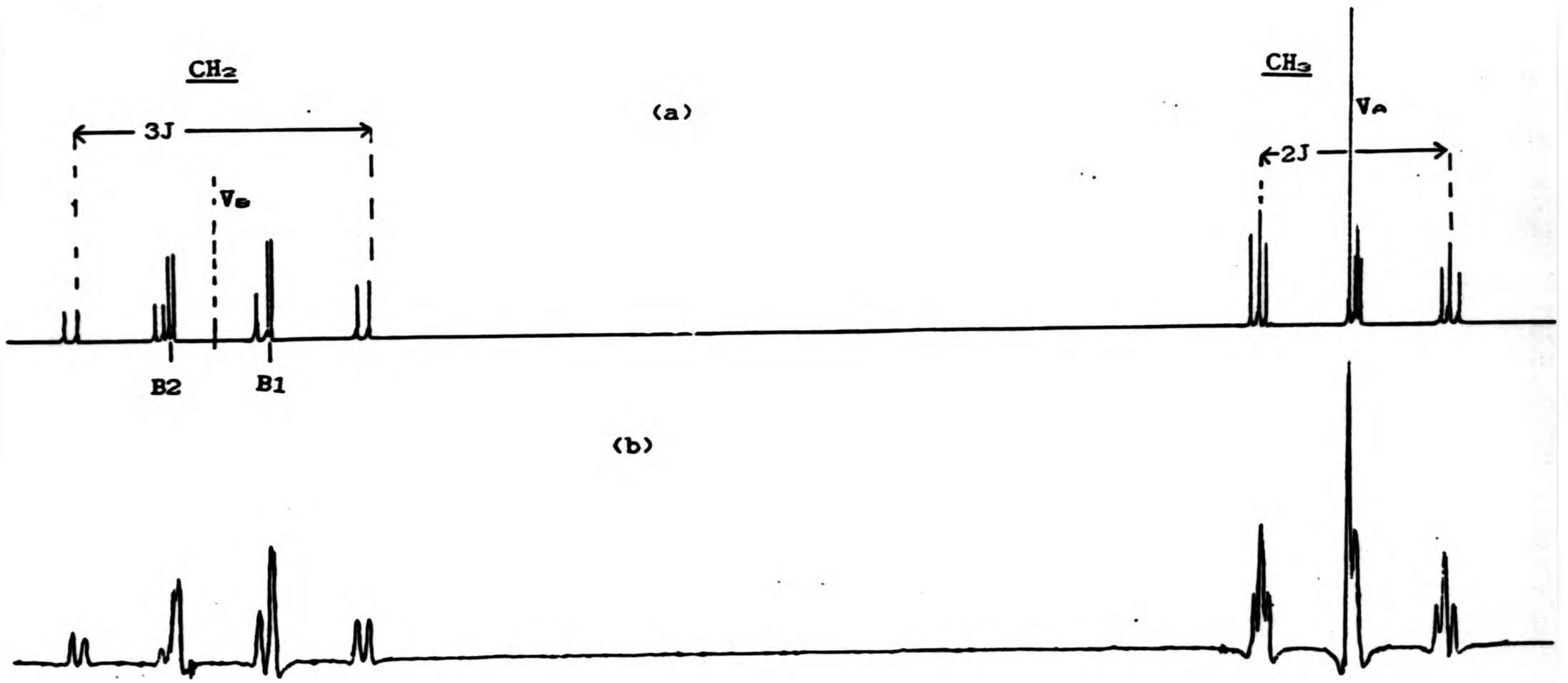


Fig 3

A_3B_2 spin simulation on $(CH_3CH_2)_3CCH_2OH$ (26) with, (a) small linewidth, and (b) resolution enhancement and correlation difference.

analysed into subspectra according to the total spin quantum number, with the total number of stationary states given by $2^{(n+m)}$ when I(A) = I(B) = 1/2. From the transition energy levels of an A_3B_2 system,[82] the spectrum can be decomposed into an a_3 subspectrum and two identical ab_2 subspectra. These subspectra together yield a strong peak at V_a, (Fig 3) corresponding to the chemical shift (Hz) of the methyl group. The position of V_b, corresponding to the methylene group chemical shift may be obtained as the midpoint between transitions B1 and B2 (Fig 3). The spin coupling constant J_{ab} can be obtained from the 3J and 2J values as shown in the spectrum (Fig 3).

2.9.2 Fast atom bombardment mass spectrometry

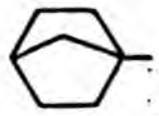
Fast Atom Bombardment Mass Spectrometry (FAB-MS) has been applied to a range of ionic, zwitterionic and thermally labile organophosphorus compounds,[84,85] and has been shown to be a potentially valuable aid to identification and characterisation of the quasiphosphonium salts: $(RO)_3PCH_2COC_6H_5$ Br^- (57), $(RO)_3PCH_2COC_6H_4Br$ Br^- (66), $(RO)_3POC(C_6H_4NO_2):CH_2$ Cl^- (63), and $(RO)_3PCH_3$ I^- (75) (R = norbornyl group, C_7H_{11}-) isolated in the present investigation. Under fast atom bombardment ionization, the quasiphosphonium salts gave intense ions corresponding to

Table 6

FAB-MS fragmentation pattern of quasiphosphonium salts:

$(RO)_2P-R'\ X^-$

A = $(RO)_2P-R'$

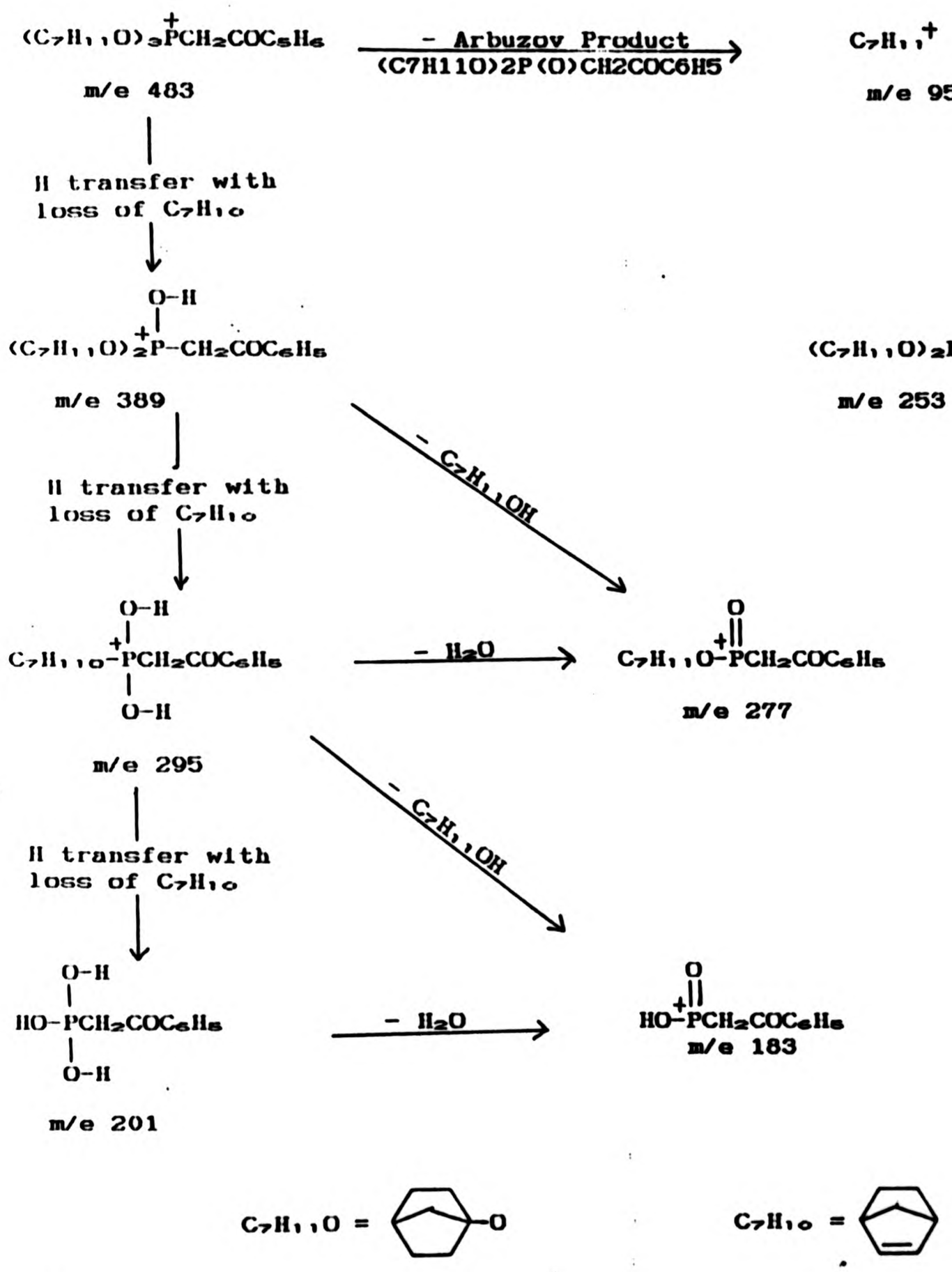
R = 

Fragment	R'		
	$CH_2COC_6H_5$	$CH_2COC_6H_4Br$	CH_3
A^+	483 (100 %)	561 / 563 (55 %)	379 (100 %)
$[A - (R-H)]^+$	389 (16 %)	467 / 469 (5 %)	285 (13 %)
$[A - (RO)_2P(O)R]^+$	95 (62 %)	95 (100 %)	95 (16 %)
$[A - (R-H) - ROH]^+$	277 (4 %)	355 / 357 (1 %)	189 (0.3 %)
$[A - 2(R-H) - H_2O]^+$	277	355 / 357	189
$[A - 2(R-H)]^+$	295 (6 %)	373 / 375 (1 %)	191 (2 %)
$[A - 3(R-H)]^+$	201 (10 %)	279 / 281 (2 %)	97 (1 %)
$[A - 3(R-H) - H_2O]^+$	183 (7 %)	261 / 263 (2 %)	
$[A - 2(R-H) - ROH]^+$	183	261 / 263	95 (16 %)
$[(RO)_2P]^+$	253 (9 %)	253 (6 %)	253 (4 %)

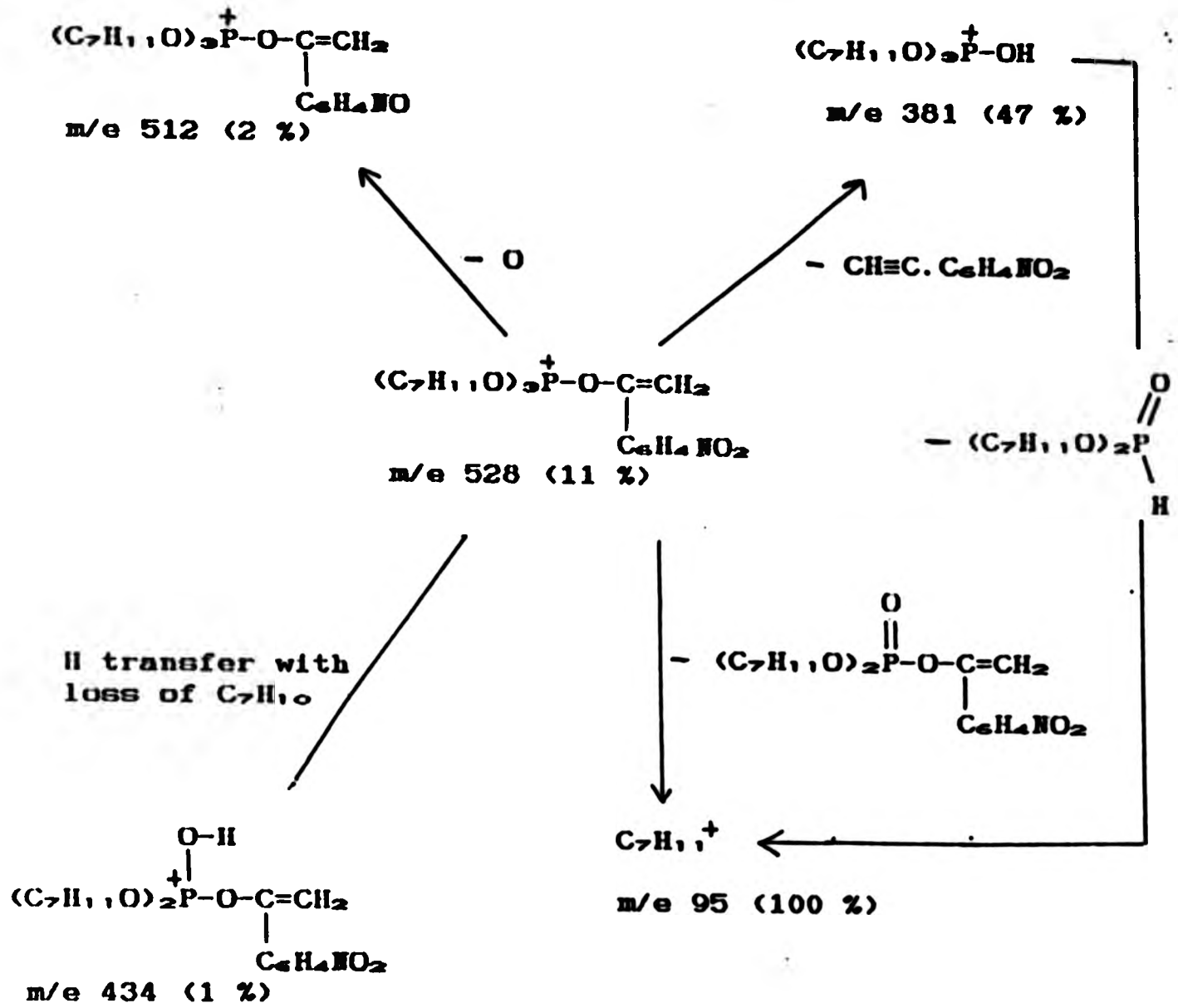
the cationic (phosphonium) part of the salt in the positive ion spectrum.

The quasiphosphonium salts 57, 66, and 75, all containing a P-C bond, undergo characteristic fragmentation as shown in Table 6 , with the fragmentation pathways of quasiphosphonium salt 57 outlined in Schemes 40. The phosphonium ions undergo two modes of fragmentation: an intramolecular proton transfer from the norbornyl group to the phosphorus-containing species with loss of C_7H_{10} (molecular weight 94) and a vapour phase Arbuzov cleavage with formation of the norbornyl cation (m/z 95) (Scheme 40). The structure of the compound C_7H_{10} (molecular weight 94) which is also lost in successive fragmentations cannot be conclusively identified, but appears to be norbornene or an isomer thereof. The relative intensity of the fragment m/z 95 obtained for the quasiphosphonium salts 57 (61.6 %) and 75 (16.3 %) reflect the differences in the thermal stabilities of the salts as observed during their decomposition (see section 2.6).

The vinyloxyphosphonium salt (63) also appeared to undergo two modes of fragmentation (Scheme 41) similar to those shown by the other phosphonium salts above, although the formation of the norbornyl cation (m/z 95), through the vapour phase Arbuzov cleavage elimination by the Perkow product route, is less likely. The fragment m/z 95 was considered to be formed by the vapour phase cleavage of the protonated trinorborn-1-yl phosphate $[(C_7H_{11}O)_3P=\overset{+}{O}H]$


(C7H11O)3PCH2COC6H5
- Arbuzov Product
(C7H11O)2P(O)CH2COC6H5
C7H11+
m/e 483
m/e 95
H transfer with loss of C7H10
O-H
(C7H11O)2P-CH2COC6H5
(C7H11O)2P+
m/e 389
m/e 253
H transfer with loss of C7H10
- C7H11OH
O-H
C7H11O-PCH2COC6H5
- H2O
O
C7H11O-PCH2COC6H5
m/e 295
m/e 277
H transfer with loss of C7H10
- C7H11OH
O-H
HO-PCH2COC6H5
- H2O
O
HO-PCH2COC6H5
m/e 201
m/e 183
C7H11O =
O
C7H10 =

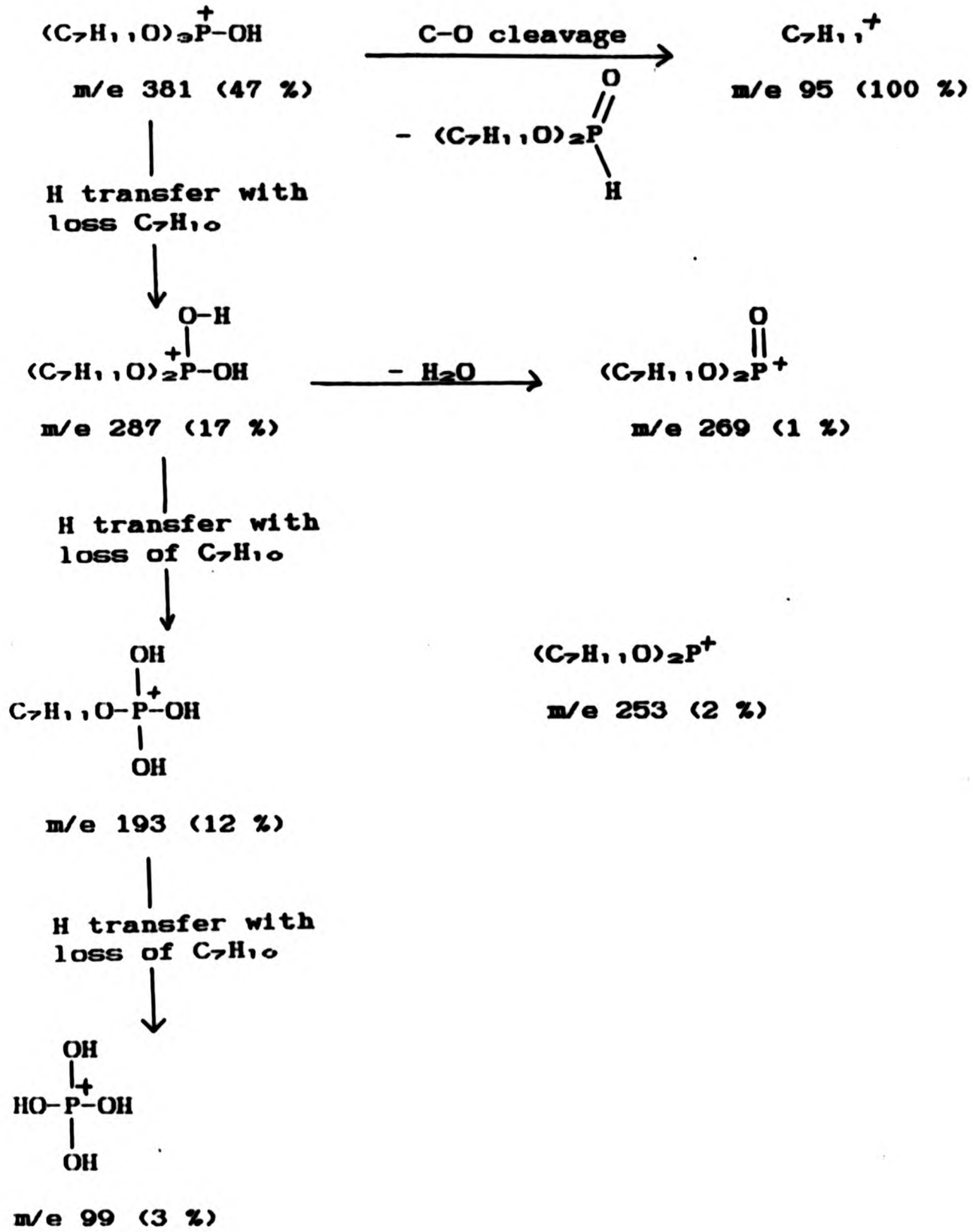
(Scheme 40)



$(C_7H_{11}O)_2P^+$

m/e 253 (1.6 %)

(Scheme 41)


$(C_7H_{11}O)_3\overset{+}{P}-OH$
C-O cleavage
$C_7H_{11}^+$
m/e 381 (47 %)
m/e 95 (100 %)
$- (C_7H_{11}O)_2P(=O)H$
H transfer with loss C_7H_{10}
$(C_7H_{11}O)_2\overset{+}{P}-OH$
$- H_2O$
$(C_7H_{11}O)_2P^+$
m/e 287 (17 %)
m/e 269 (1 %)
H transfer with loss of C_7H_{10}
$C_7H_{11}O-\overset{+}{P}(OH)-OH$
$(C_7H_{11}O)_2P^+$
m/e 193 (12 %)
m/e 253 (2 %)
H transfer with loss of C_7H_{10}
$HO-\overset{+}{P}(OH)-OH$
m/e 99 (3 %)

(Scheme 42)

(Scheme 42), itself being formed as shown in Scheme 41 by a process similar to the bimolecular trans-elimination reaction observed during thermal decomposition of the vinyloxyphosphonium salt (63) (see section 2.6).

2.9.3 X-ray Crystallography

X-ray structure determinations of the phosphonium salts, trinorborn-1-yloxy(phenacyl)phosphonium bromide (57) and trinorborn-1-yloxy-1-(p-nitrophenyl)vinyloxyphosphonium chloride (63), were carried out in order to establish the structures of the salts in the solid state and also to establish the bond lenghts and angles around the phosphorus atom. Such measurements might help to elucidate the cause of the shielding effect (upfield shift) obeserved in the ^{31}P n.m.r. spectra of the phosphonium bromide (57) the phosphonates and phosphate derived from trinorborn-1-yl phosphite (see Table 2). The bond lenghts and angles of the phosphonium bromide (57) and chloride (63) with estimated standard deviations in parentheses, are shown in Tables 7 to 10. The crystal structures are pictorically represented in Figures 4 to 7, and the schematic representation of the bonds and angles around the phosphorus are shown in Figure 8.

The X-ray structures of the phosphonium salts, 57, and 63, clearly showed that the compounds are phosphonium salts

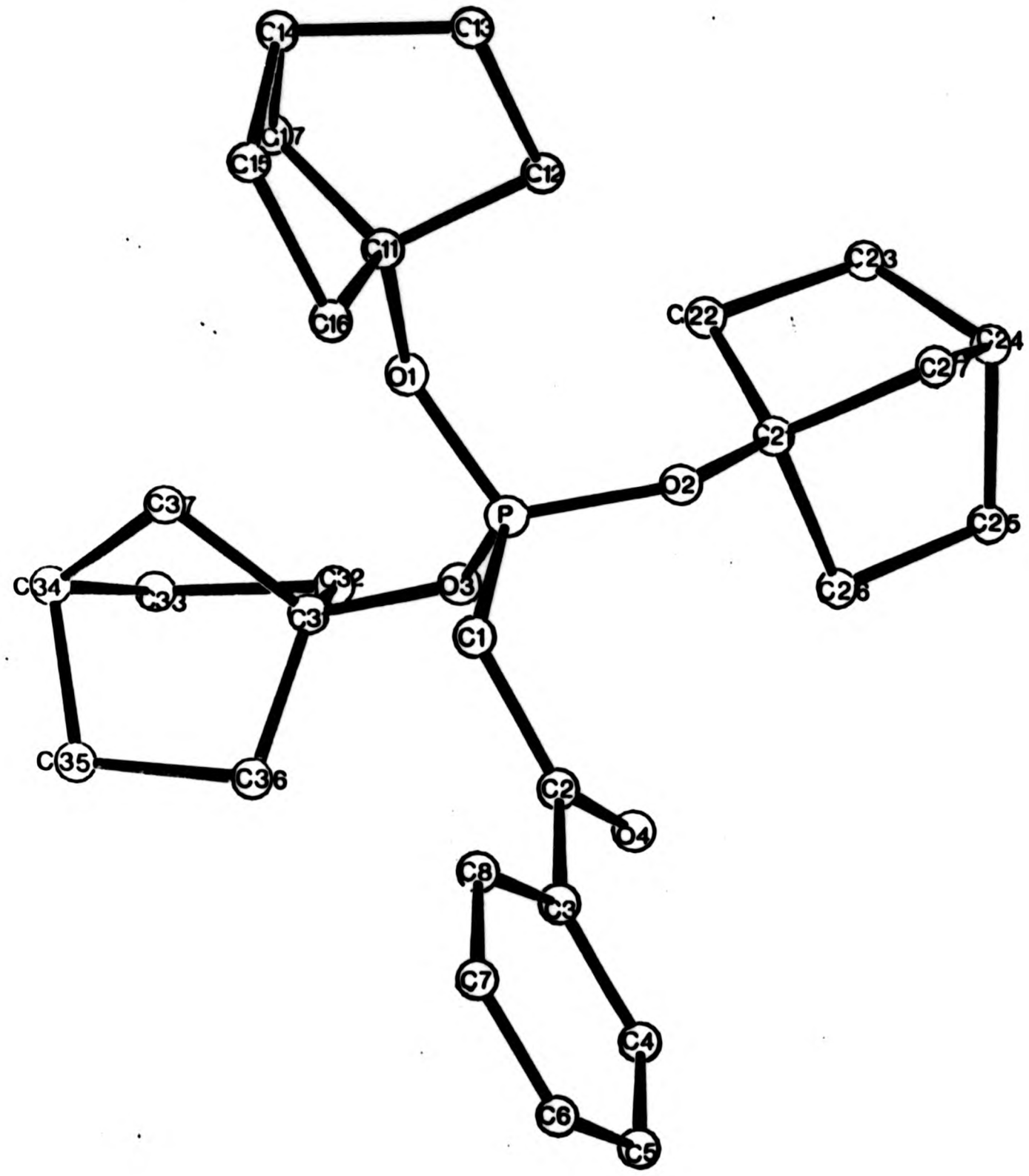


Fig 4

X-ray crystal structure of the phenacylphosphonium bromide (57) without the bromide ion, and showing the crystallographic numbering scheme used.

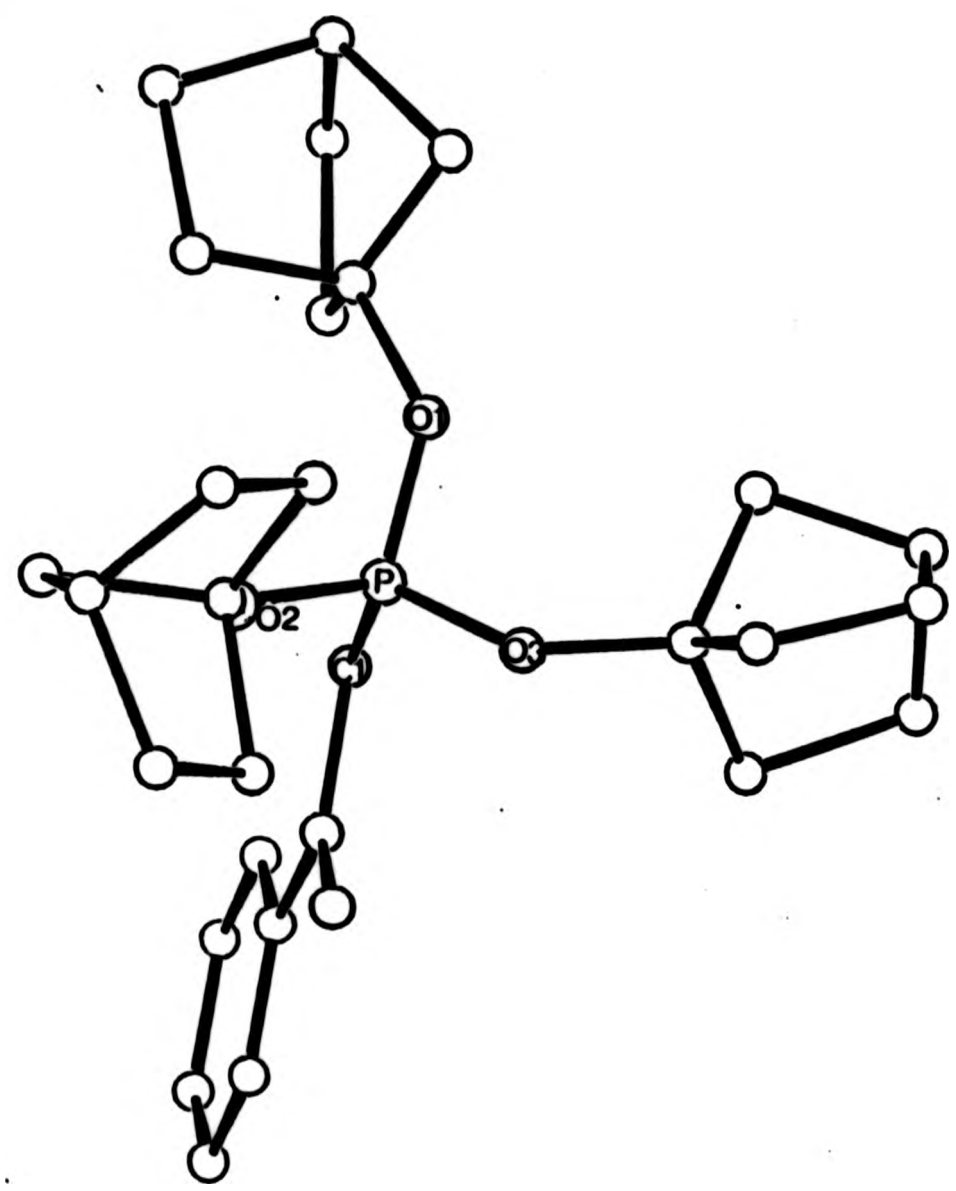


Fig 5

X-ray crystal structure of the phenacylphosphonium bromide (57) with the bromide ion.

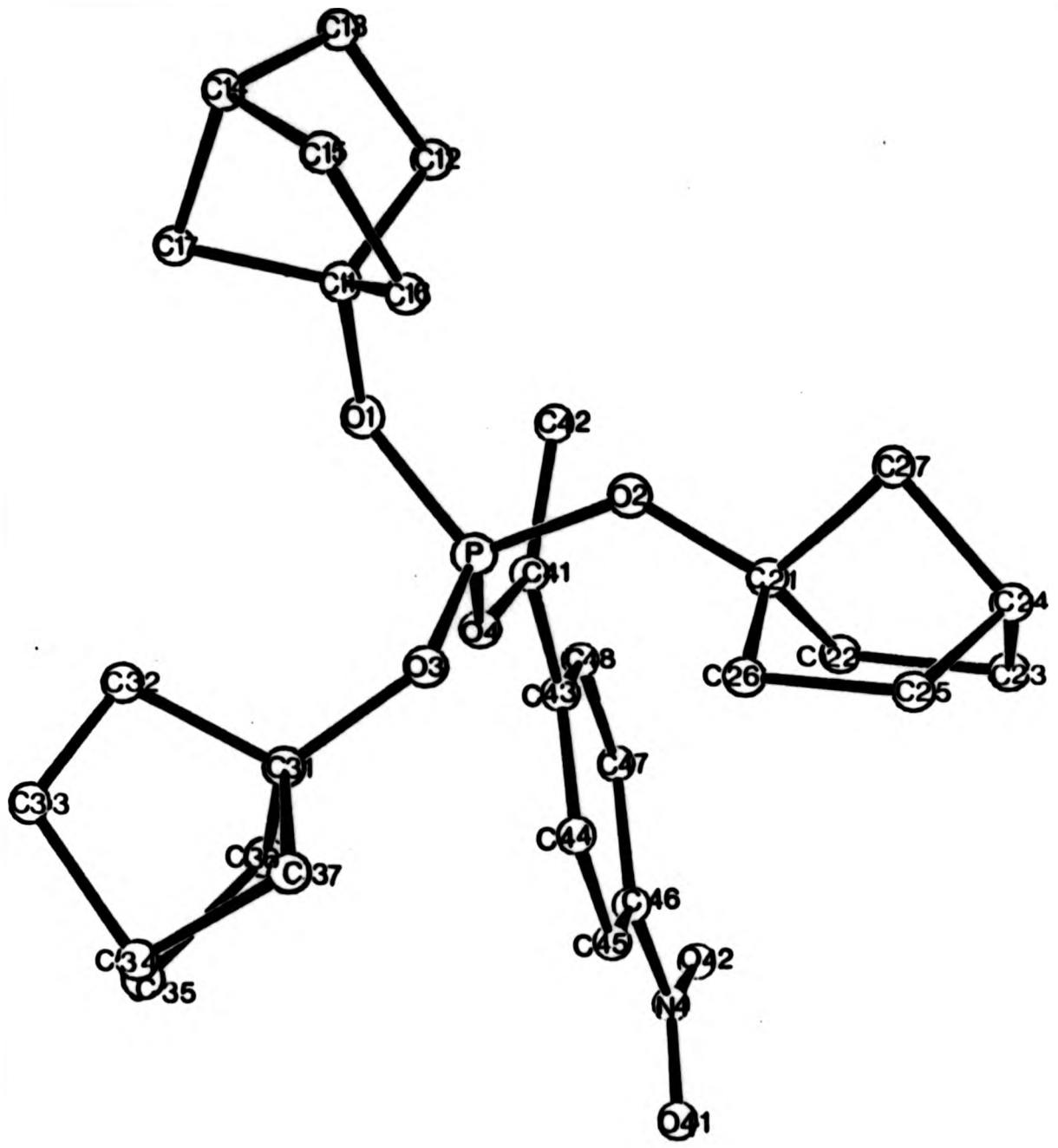


Fig 6

X-ray crystal structure of the vinyloxyphosphonium chloride (63) showing the crystallographic numbering scheme used.

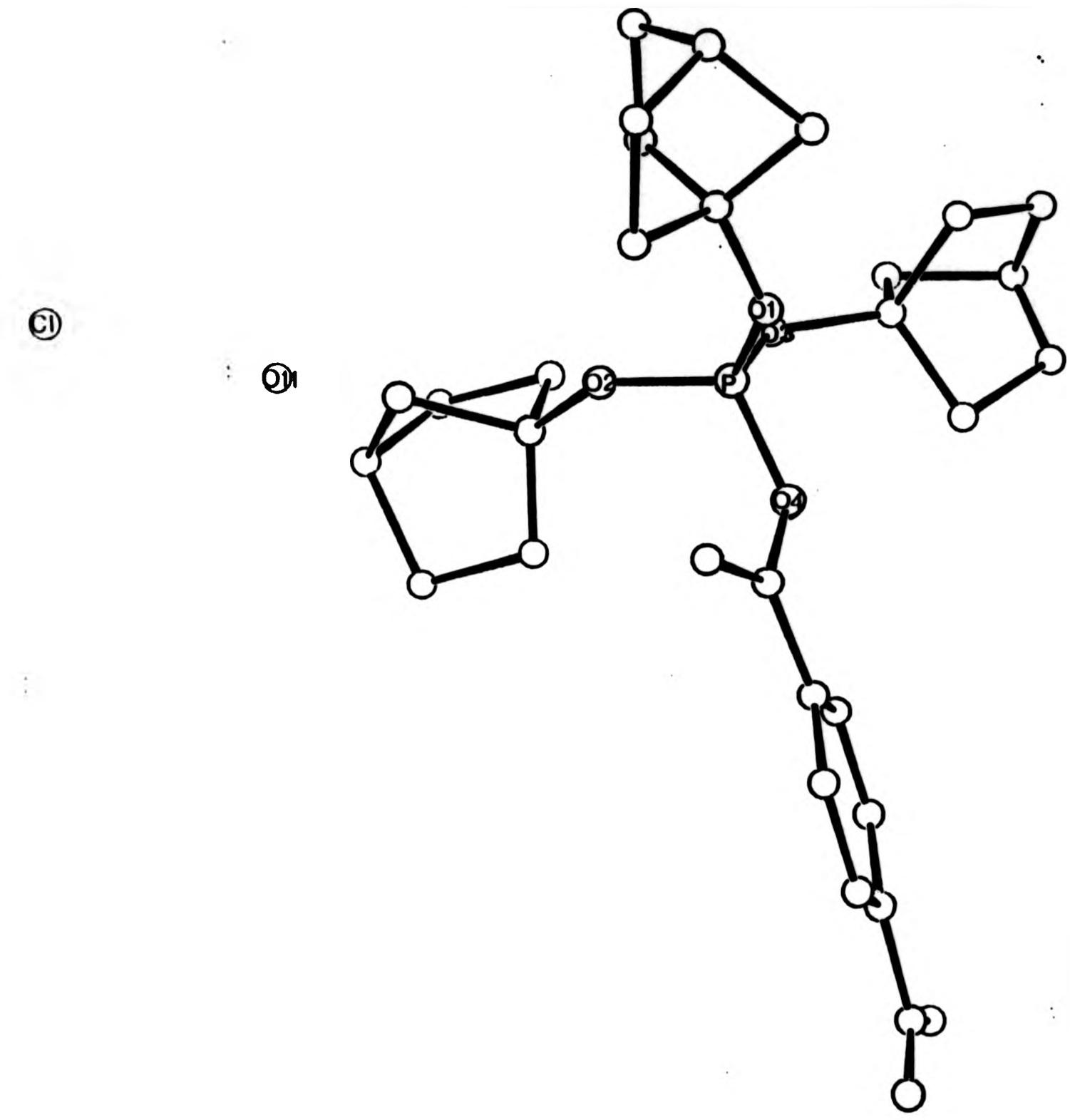


Fig 7

X-ray crystal structure of the vinyloxyphosphonium chloride (63).

composed of tetrahedral cations with a $P^{+}...Br^{-}$ distance of 4.58 Å and $P^{+}...Cl^{-}$ distance of 4.71 Å. There is no significant difference between the P-O bond lengths around the tetrahedral phosphorus in the two structures. Mean lengths of 1.527(13) Å and 1.541(23) Å were obtained for the phosphonium bromide (57) and the phosphonium chloride (63)

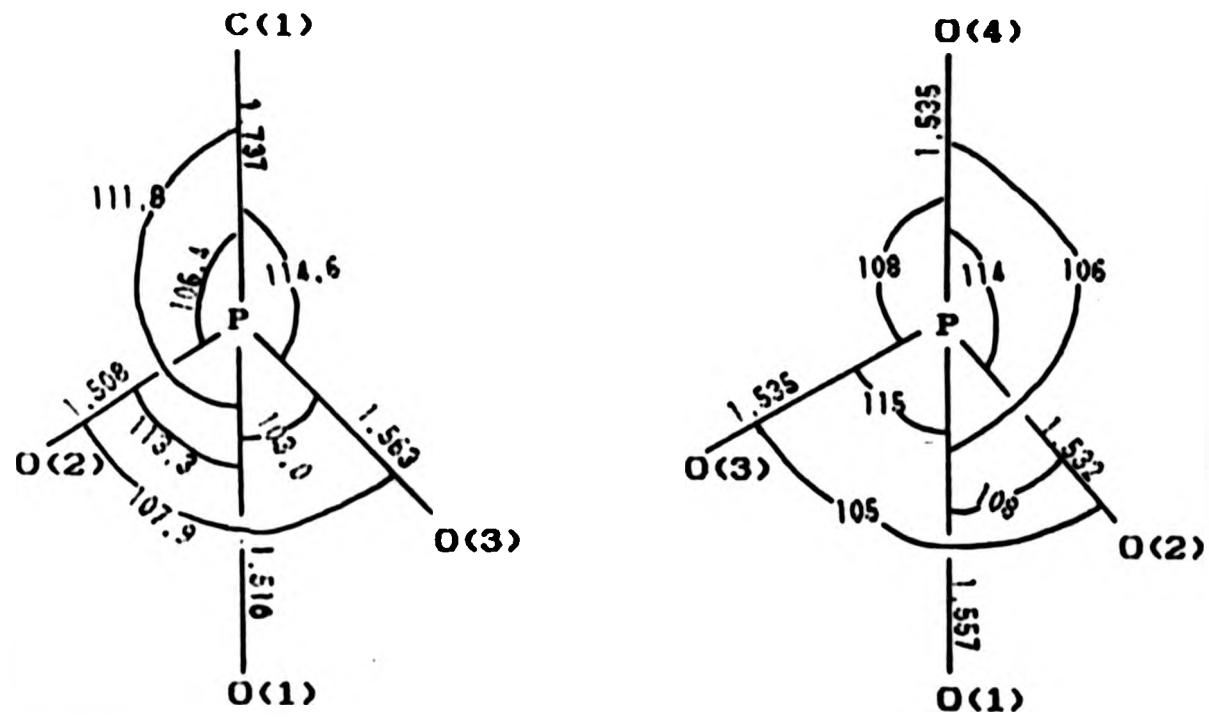


Fig 8: Schematic representation of the bonds around the phenacylphosphonium bromide (57) and vinyloxyphosphonium chloride (63) respectively.

respectively which are in good agreement with the values observed previously for certain quasiphosphonium salts, 1.54 - 1.57 Å,[86] and for organic orthophosphates.[87]

There is some distortion from the ideal tetrahedral angle at the phosphorus atom (Fig 8). A distortion towards C3v symmetry is expected in the two structures due to the

three bulky norbornyl groups. The distortion around the phosphorus atom in the vinyloxyphosphonium chloride (63) appeared to be towards a C2v symmetry, two opposite angles being larger than the ideal tetrahedral value, 109.4°, while the remaining four are smaller. The distortion in the phenacylphosphonium bromide (57) appeared not to conform to either the C3v or the C2v symmetry. Three angles are larger than the ideal tetrahedral value, and three are smaller. Close intermolecular H...O, and H...C contacts between the groups, of 2.76 - 2.87 Å are found only between the smaller angles in the two structures.

An additional peak that appeared to be due to an oxygen atom from its electron density, was obtained in the phosphonium chloride (63) structure. It was assumed to be that from a water molecule, though the hydrogen atoms were not located. There was no indication of intramolecular close contact to suggest hydrogen bonding.

Table 7

Bond lenghts (Å) for trinorborn-1-yloxy(phenacyl)-phosphonium bromide (57)

P	-O(1)	1.510(13)	P	-O(2)	1.508(14)
P	-O(3)	1.563(13)	P	-C(1)	1.737(20)
O(1)	-C(11)	1.469(24)	O(2)	-C(21)	1.47(3)
O(3)	-C(31)	1.429(23)	O(4)	-C(2)	1.22(3)
C(1)	-C(2)	1.50(3)	C(2)	-C(3)	1.48(3)
C(4)	-C(5)	1.395(18)	C(4)	-C(3)	1.395(19)
C(5)	-C(6)	1.395(18)	C(6)	-C(7)	1.395(19)
C(7)	-C(8)	1.395(16)	C(8)	-C(3)	1.395(18)
C(11)	-C(12)	1.51(4)	C(11)	-C(16)	1.52(3)
C(11)	-C(17)	1.44(3)	C(12)	-C(13)	1.59(4)
C(13)	-C(14)	1.59(4)	C(14)	-C(15)	1.43(4)
C(14)	-C(17)	1.63(4)	C(15)	-C(16)	1.57(4)
C(21)	-C(22)	1.45(3)	C(21)	-C(26)	1.57(3)
C(21)	-C(27)	1.55(4)	C(22)	-C(23)	1.55(4)
C(23)	-C(24)	1.43(4)	C(24)	-C(25)	1.56(4)
C(24)	-C(27)	1.57(4)	C(25)	-C(26)	1.52(4)
C(31)	-C(32)	1.53(3)	C(31)	-C(36)	1.49(3)
C(31)	-C(37)	1.51(3)	C(32)	-C(33)	1.52(4)
C(33)	-C(34)	1.52(4)	C(34)	-C(35)	1.52(4)
C(34)	-C(37)	1.56(4)	C(35)	-C(36)	1.54(4)

Table 8

Bond lenghts (Å) for trinorborn-1-yloxy-1-(p-nitrophenyl)vinyloxyphosphonium chloride (63)

P(1)	-O(1)	1.557(24)	P(1)	-O(2)	1.532(22)
P(1)	-O(3)	1.535(22)	P(1)	-O(4)	1.535(21)
O(1)	-C(11)	1.42(4)	O(2)	-C(21)	1.44(4)
O(3)	-C(31)	1.53(4)	O(4)	-C(41)	1.40(3)
C(11)	-C(12)	1.56(4)	C(11)	-C(16)	1.54(4)
C(11)	-C(17)	1.47(4)	C(12)	-C(13)	1.55(5)
C(13)	-C(14)	1.43(5)	C(14)	-C(15)	1.56(5)
C(14)	-C(17)	1.61(5)	C(15)	-C(16)	1.54(4)
C(21)	-C(22)	1.45(4)	C(21)	-C(26)	1.49(4)
C(21)	-C(27)	1.59(4)	C(22)	-C(23)	1.53(5)
C(23)	-C(24)	1.63(6)	C(24)	-C(25)	1.42(6)
C(24)	-C(27)	1.58(6)	C(25)	-C(26)	1.50(5)
C(31)	-C(32)	1.58(5)	C(31)	-C(36)	1.50(4)
C(31)	-C(37)	1.38(4)	C(32)	-C(33)	1.35(4)
C(33)	-C(34)	1.63(6)	C(34)	-C(35)	1.19(5)
C(34)	-C(37)	1.54(5)	C(35)	-C(36)	1.69(5)
C(41)	-C(42)	1.41(4)	C(41)	-C(43)	1.54(4)
C(43)	-C(44)	1.395(1)	C(43)	-C(48)	1.395(1)
C(44)	-C(45)	1.395(1)	C(45)	-C(46)	1.395(1)
C(46)	-C(47)	1.395(1)	C(46)	-N(4)	1.46(3)
C(47)	-C(48)	1.395(1)	N(4)	-O(41)	1.20(4)
N(4)	-O(42)	1.16(3)			

Table 9

Bond angles (°) for trinorborn-1-yloxy(phenacyl)-phosphonium bromide (57)

O(2)	-P	-O(1)	113.3(8)	O(3)	-P	-O(1)	103.0(7)
O(3)	-P	-O(2)	107.9(7)	C(1)	-P	-O(1)	111.8(8)
C(1)	-P	-O(2)	106.4(9)	C(1)	-P	-O(3)	114.6(8)
C(11)	-O(1)	-P	134(1)	C(21)	-O(2)	-P	127(1)
C(31)	-O(3)	-P	133(1)	C(2)	-C(1)	-P	115(1)
C(1)	-C(2)	-O(4)	122(2)	C(3)	-C(2)	-O(4)	117(2)
C(3)	-C(2)	-C(1)	121(2)	C(3)	-C(4)	-C(5)	120(1)
C(6)	-C(5)	-C(4)	120(1)	C(7)	-C(6)	-C(5)	120(1)
C(8)	-C(7)	-C(6)	120(1)	C(3)	-C(8)	-C(7)	120(1)
C(4)	-C(3)	-C(2)	119(1)	C(8)	-C(3)	-C(2)	121(1)
C(8)	-C(3)	-C(4)	120(1)	C(12)	-C(11)	-O(1)	111(2)
C(16)	-C(11)	-O(1)	114(2)	C(16)	-C(11)	-C(12)	106(2)
C(17)	-C(11)	-O(1)	111(2)	C(17)	-C(11)	-C(12)	102(2)
C(17)	-C(11)	-C(16)	111(2)	C(13)	-C(12)	-C(11)	101(2)
C(14)	-C(13)	-C(12)	103(2)	C(15)	-C(14)	-C(13)	95(2)
C(17)	-C(14)	-C(13)	100(2)	C(17)	-C(14)	-C(15)	97(2)
C(16)	-C(15)	-C(14)	114(2)	C(15)	-C(16)	-C(11)	94(2)
C(14)	-C(17)	-C(11)	96(2)	C(22)	-C(21)	-O(2)	121(2)
C(26)	-C(21)	-O(2)	108(2)	C(26)	-C(21)	-C(22)	111(2)
C(27)	-C(21)	-O(2)	109(2)	C(27)	-C(21)	-C(22)	105(2)
C(27)	-C(21)	-C(26)	100(2)	C(23)	-C(22)	-C(21)	101(2)
C(24)	-C(23)	-C(22)	107(2)	C(25)	-C(24)	-C(23)	109(2)
C(27)	-C(24)	-C(23)	102(2)	C(27)	-C(24)	-C(25)	97(2)
C(26)	-C(25)	-C(24)	106(2)	C(25)	-C(26)	-C(21)	101(2)
C(24)	-C(27)	-C(21)	92(2)	C(32)	-C(31)	-O(3)	108(2)

Table 9 continued

C(36) -C(31) -O(3)	112(2)	C(36) -C(31) -C(32)	111(2)
C(37) -C(31) -O(3)	120(2)	C(37) -C(31) -C(32)	102(2)
C(37) -C(31) -C(36)	104(2)	C(33) -C(32) -C(31)	98(2)
C(34) -C(33) -C(32)	110(2)	C(35) -C(34) -C(33)	98(2)
C(37) -C(34) -C(33)	98(2)	C(37) -C(34) -C(35)	99(2)
C(36) -C(35) -C(34)	108(2)	C(35) -C(36) -C(31)	100(2)
C(34) -C(37) -C(31)	96(2)		

Table 10

Bond angles (°) for trinorborn-1-yloxy-1-(p-nitrophenyl)vinyloxyphosphonium chloride (63)

O(2)	-P(1)	-O(1)	106(1)	O(3)	-P(1)	-O(1)	115(1)
O(3)	-P(1)	-O(2)	105(1)	O(4)	-P(1)	-O(1)	106(1)
O(4)	-P(1)	-O(2)	114(1)	O(4)	-P(1)	-O(3)	102(1)
C(11)	-O(1)	-P(1)	131(2)	C(21)	-O(2)	-P(1)	129(2)
C(31)	-O(3)	-P(1)	130(2)	C(41)	-O(4)	-P(1)	127(2)
C(12)	-C(11)	-O(1)	106(3)	C(16)	-C(11)	-O(1)	113(3)
C(16)	-C(11)	-C(12)	107(3)	C(17)	-C(11)	-O(1)	110(3)
C(17)	-C(11)	-C(12)	113(3)	C(17)	-C(11)	-C(16)	107(3)
C(13)	-C(12)	-C(11)	92(3)	C(14)	-C(13)	-C(12)	110(4)
C(15)	-C(14)	-C(13)	104(4)	C(17)	-C(14)	-C(13)	104(3)
C(17)	-C(14)	-C(15)	101(3)	C(16)	-C(15)	-C(14)	104(3)
C(15)	-C(16)	-C(11)	97(3)	C(14)	-C(17)	-C(11)	87(3)
C(22)	-C(21)	-O(2)	116(3)	C(26)	-C(21)	-O(2)	112(3)
C(26)	-C(21)	-C(22)	111(3)	C(27)	-C(21)	-O(2)	109(3)
C(27)	-C(21)	-C(22)	106(3)	C(27)	-C(21)	-C(26)	101(3)
C(23)	-C(22)	-C(21)	106(3)	C(24)	-C(23)	-C(22)	101(4)
C(25)	-C(24)	-C(23)	108(5)	C(27)	-C(24)	-C(23)	101(4)
C(27)	-C(24)	-C(25)	98(5)	C(26)	-C(25)	-C(24)	112(5)
C(25)	-C(26)	-C(21)	98(3)	C(24)	-C(27)	-C(21)	90(4)
C(32)	-C(31)	-O(3)	114(3)	C(36)	-C(31)	-O(3)	114(3)
C(36)	-C(31)	-C(32)	107(3)	C(37)	-C(31)	-O(3)	112(3)
C(37)	-C(31)	-C(32)	102(3)	C(37)	-C(31)	-C(36)	107(3)
C(33)	-C(32)	-C(31)	99(4)	C(34)	-C(33)	-C(32)	111(4)
C(35)	-C(34)	-C(33)	93(4)	C(37)	-C(34)	-C(33)	94(4)
C(37)	-C(34)	-C(35)	107(5)	C(36)	-C(35)	-C(34)	111(4)

Table 10 continued

C(35)	-C(36)	-C(31)	91(3)	C(34) -C(37) -C(31)	97(3)
C(42)	-C(41)	-O(4)	124(3)	C(43) -C(41) -O(4)	109(3)
C(43)	-C(41)	-C(42)	126(3)	C(44) -C(43) -C(41)	122(2)
C(46)	-C(43)	-C(41)	118(2)	C(48) -C(43) -C(44)	120.0(1)
C(45)	-C(44)	-C(43)	120.0(1)	C(46) -C(45) -C(44)	120.0(1)
C(47)	-C(48)	-C(45)	120.0(1)	N(4) -C(46) -C(45)	123(2)
N(4)	-C(46)	-C(47)	117(2)	C(48) -C(47) -C(46)	120.0(1)
C(47)	-C(48)	-C(43)	120.0(1)	O(41) -N(4) -C(46)	111(3)
O(42)	-N(4)	-C(46)	116(4)	O(42) -N(4) -O(41)	131(4)

Chapter 3

EXPERIMENTAL

Melting points were determined with a Gallenkamp melting point apparatus, and are uncorrected. Infrared spectra were determined with Perkin-Elmer 781 Infrared spectrometer.

^{31}P and ^{13}C NMR spectra were recorded on a Bruker WP-80 instrument operating at 32.4 MHz and 20.12 MHz respectively. ^{1}H NMR spectra were recorded on Perkin-Elmer R12B at 60 MHz. Chemical shifts are given relative to 85 % H_3PO_4 (^{31}P) and to TMS (^{1}H and ^{13}C), with downfield positive. Quantitative data based on ^{31}P NMR are calculated from the proton decoupled spectra unless where specified. Spectral abbreviations used are: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and dist. = distorted.

The FAB mass spectra were obtained using a glycerol matrix on a VG Analytical ZAB-IF spectrometer. A primary beam of xenon atoms of 2-8 keV was employed.

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3.1 Preparations of alcohols: 2,2-diethylbutan-1-ol (26), 2,2,2-triphenylethanol (27) and norbornan-1-ol (29).

Dimesylate of 2,2-diethylpropane-1,3-diol:[28]

Methanesulphonyl chloride (165 g, 1.44 mol) was added to a stirred solution of 2,2-diethyl-1,3-propanediol (95 g, 0.72 mol) in dried pyridine (400 cm^3) cooled to -10 °C over a period of one hour; with the temperature kept below 5 °C during the addition. The mixture was allowed to stand below 0 °C for 18 h after the addition and then poured on to crushed ice (500 g) to yield solid which was filtered off, washed several times with water and dried. Recrystallization from methanol gave the dimesylate as white needles (192 g, 92.6 %), m.p. 90 - 92 °C (lit.[27] 92.5 - 94.5 °C), ν_{max} (KBr disc) 2980 (C-H), 1350, 1180 (SO_2), 1000 - 840 (S-O-C) cm^{-1}, m/z 179 (10.4 %), 109 (13.5 %), 79 (100 %), δ_H ($CDCl_3$) 0.88 (dist. t, 6H, $C-CH_3$), 1.25 - 1.6 (m, 4H, CCH_2C), 3.04 (s, 6H, SO_2CH_3), 4.04 (s, 4H, CH_2OSO_2).

5,5-Diethyl-1,2-oxathiane-2,2-dioxide (31):[27]

n-Butyllithium in hexane (2.5 M, 95 cm^3) was added to a stirred solution of dimesylate of 2,2-diethylpropane-1,3-diol (62 g, 0.215mol) in anhydrous tetrahydrofuran (800 cm^3)

at -73 °C over a period of one hour under nitrogen. The reaction mixture was stirred for a further 2 h at -73 °C and then allowed to stand at room temperature for 72 h. Water (100 cm^3) was added slowly, and the organic phase was separated, washed with water (100 cm^3) followed by saturated sodium chloride solution (50 cm^3), and dried ($MgSO_4$). Removal of the solvent gave a brown oil (42 g). Column chromatography of the oil on silica gel (100 - 120 mesh) and elution with pentane-ether (1:1) afforded a clear yellow oil which on distillation at 128 °C / 0.7 mm (lit.[27] 98 °C / 0.06 mm) gave the oxathiane dioxide (36) (29.8 g, 72 %), ν_{max} (liquid film) 2980 (C-H), 1465 (ring CH_2O), 1360, 1170 (SO_2), m/z 192 (M+, 0.2 %), 110 (8.7 %), 98 (36 %), 97 (100 %) 96 (43 %), 54 (77 %), δ_H ($CDCl_3$) 0.84 (dist.t, 6H, CH_3), 1.26 - 1.65 (m, 4H, $\underline{CH_2}CH_3$), 1.98 (dist.t, 2H, C-$\underline{CH_2}$-CH_2S), 3.14 (dist.t, 2H, CH_2SO_2), 4.2 (s, 2H, CH_2OSO_2).

<u>2,2-Diethylbutan-1-ol (26):[27]</u>

Aluminium chloride (38.9 g, 0.292 mol) was added to a cooled solution of anhydrous ether (200 cm^3) under nitrogen with stirring. Lithium aluminium hydride (44.3 g, 1.17 mol) in anhyrdous 1,4-dioxane (1 L) was added slowly to the cooled ether mixture which was then stirred for a further 15 min after the addition. 5,5-Diethyl-1,2-oxathiane-2,2-

dioxide (30 g, 0.16 mol) in anhydrous dioxane (100 cm^3) was added and the reaction mixture was heated under reflux for 90 h. The mixture was cooled in ice and then hydrochloric acid (10 %, 100 cm^3) was added cautiously. The precipitate was filtered off, dissolved in hydrochloric acid (30 %) and the solution extracted with dichloromethane (2 × 200 cm^3) and ether (200 cm^3). The organic extracts were combined, washed with saturated sodium chloride solution (100 cm^3) and dried ($MgSO_4$). Removal of solvent and distillation at 96 - 98 °C / 25 mm (lit.[27] 65 °C / 18 mm) gave the alcohol (26) (2.92 g, 14.4 %) as a clear oil, ν_{max} (liquid film) 3380 - 3340 (br, OH), 2970, 2930, 1460 cm^{-1}, δ_C ($CDCl_3$) 7.4 (CH_3), 25.1 ($-CH_2$) 39.6 ($\underline{C}-CH_2O$), 65.9 (CH_2-OH).

A second fraction at 120 - 125 °C / 25 mm gave 2,2-diethyl-4-mercapto-butan-1-ol (8.06 g, 31.8 %), m/z 162 (M^+, 2.2 %), 129 (3.8 %), 113 (11.5 %), 111 (10.4 %), 56 (100 %). Stirring in absolute alcohol with Raney nickel afforded 2,2-diethylbutan-1-ol (5.2 g, 81 %), with identical ^1H n.m.r. spectrum to the above.

Triphenylacetic acid (33):[26]

Magnesium turnings (25 g, 1.03 mol) and iodine (9 g, 0.07 mol) in anhydrous ether (1 L) were stirred at room temperature under dried nitrogen until the iodine colour disappeared. The stirred mixture was then cooled in ice and

triphenylmethyl chloride (147.2 g, 0.53 mol) was added in one portion. Cooling was continued for a further 30 min after addition the mixture was then allowed to attain room temperature and was heated under reflux (4 h). The reaction mixture was allowed to cool to room temperature and dry CO_2 gas was bubbled into the stirred mixture (6 h). The resulting mixture was hydrolysed by the addition of dilute hydrochloric acid (50 %, 1 L) and then cooled in ice. The yellow solid which formed was filtered off, washed with water and digested on a steam bath (2 h) in hydrochloric acid (20 %, 600 cm^3). The solid was filtered off, washed several times with water and then digested on a steam bath (3 h) in sodium hydroxide solution (10 %, 800 cm^3). Water (2.5 L) was added to the cooled mixture to dissolve the sodium salt and the solution was filtered on a sintered glass funnel, and washed with water until most of the remaining solid dissolved. The filtrate was acidified with concentrated hydrochloric acid and the mixture heated on a steam bath (2 h) to coagulate the precipitated acid. The precipitate was filtered off, washed with water, dried and recrystallised from ethanol to afford the acid (31) (108 g, 71 %), m.p. 260 - 263 °C (lit.[28] 269 - 270 °C), δ_H (DMSO-d_6) 7.2 (m, Ar), 13.1 (br, -COOH), δ_C (DMSO-d_6) 174.4 (CO), 143.3 (ArC-1), 129.9 (ArC-2), 127.6 (ArC-2,6), 126.6 (ArC-3,5) 66.9 (Ph_3C), ν_{max} (KBr disc) 3300 (OH), 2915 (C-H), 1685 (C=O) cm^{-1}.

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2.2.2-Triphenylethanol (27):

Triphenylacetic acid (50 g, 0.14 mol) in anhydrous tetrahydrofuran (250 cm^3) was added dropwise to a stirred solution of lithium aluminium hydride (10 g, 0.27 mol) in tetrahydrofuran (1 L) under dried nitrogen at room temperature and the mixture refluxed for 24 h. The reaction mixture was cooled to room temperature and water (25 cm^3) was cautiously added dropwise with stirring, to decompose the excess lithium aluminium hydride. Dilute sulphuric acid was then added to dissolve the lithium complex and the organic phase was separated. The aqueous phase was extracted with tetrahydrofuran (2 × 100 cm^3) and the combined organic extract was washed with sodium hydroxide solution (10 %, 100 cm^3), saturated sodium chloride solution (100 cm^3) and dried ($MgSO_4$). Evaporation of the solvent gave a yellow solid which on decolourization with animal charcoal and recrystallization from hexane afforded the alcohol (24.3 g, 51 %), m.p. 103 - 104 °C (lit.[20] 104 - 105 °C), (Found: C, 87.4; H, 6.6; $C_{20}H_{18}O$ requires C, 87.5; H, 6.6 %). δ_H ($CDCl_3$) 7.2 (s, 15H, Ar), 4.6 (s, 2H, CH_2), 1.6 (s, 1H, OH), δ_C ($CDCl_3$) 145.3 (Ar C-1), 129.6 (Ar C-4), 128.3 (Ar C-2,6), 126.7 (ArC-3,5), 70.4 (CH_2OH), 58.9 (Ph_3C), ν_{max} (KBr disc) 3360 (OH), 1590 (C=C) cm^{-1}.

Attempts to use ethyl acetate to decompose the excess lithium aluminium hydride resulted in the formation of 2,2,2-triphenylethyl acetate, δ_H ($CDCl_3$) 7.2 (s, 15H, Ar),

5.1 (s, 2H, CH_2O), 1.85 (s, 3H, $COCH_3$), δ_C ($CDCl_3$) 170.9 (CO), 145.0 (Ar C-1), 129.38 (Ar C-2,6), 128.1 (ArC-3,5), 126.7 (ArC-4), 70.3 (CH_2O), 56.8 (Ph_3C), 20.9 ($COCH_3$).

2-Norbornene-5-endo-carboxylic acid:[82]

Freshly distilled cyclopentadiene (99.4 g, 1.51mol) was added slowly to a stirred solution of acrylic acid (108.6 g, 1.51 mol) in anhydrous ether (200 cm^3) cooled in ice. The cooled mixture was stirred for a further 3 h, then allowed to attain room temperature and left stirring for 18 h. Excess cyclopentadiene and ether were distilled, and the residue distilled at 118 - 120 °C / 1 mm (lit.[82] 132 - 134 °C / 22 mm) to afford the acid (158.2 g, 75.9 %) as a clear liquid, δ_H (CCl_4) 11.7 (s, COOH), 6.0 (m, 2H, CH=CH), 2.8 - 3.2 (m, 3H, C-1,4,5), 1.3 - 2.3 (m, 4H, C-6,7).

2-Endo-norbornane carboxylic acid:

2-Norbornene-5-endo-carboxylic acid (58 g, 0.42 mol) in absolute alcohol (150 cm^3) was hydrogenated in the presence of 5 % palladium on charcoal catalyst (1.5 g) at 3 atm pressure for one hour. Filtration of the catalyst and drying of the filtrate ($MgSO_4$) gave on evaporation of the solvent the acid (53.7 g, 91.3 %) as a white solid, m.p.

52 - 57 °C (lit.[59] 65 °C), δ_H (CCl_4) 11.8 (s, COOH), 2.1 - 2.9 (m, 3H, C-1,2,4), 1.2 - 2.0 (m, 8H, C-3,5,6,7).

2-Exo-bromonorbornane-1-carboxylic acid (36):[60]

2-Endo-norbornane carboxylic acid (53.7 g, 0.3 mol), bromine (73.6 g, 0.46 mol) and phosphorus trichloride (2ml) were heated in an oil bath between 80 - 90 °C (8 h). The reaction mixture, which solidified on cooling, was triturated with light petroleum to afford a white solid. Recrystallization from toluene gave the acid (40 g, 47.6 %), m.p. 138 - 140 °C (lit.[60] 140 - 143 °C), m/z 220 and 218 (M^+, 2.5 and 2.1 %), 139 (100 %), 110 (18.9 %), δ_C ($CDCl_3$) 29.2 (C-5), 32.6 (C-6), 36.7 (C-4), 36.9 (C-7), 43.9 (C-3), 53.0 (C-2), 59.1 (C-1), 179.7 (COOH), δ_H ($CDCl_3$) 1.25 - 2.3 (m, 9H), 4.2 (m, 1H, C-2), 12.0 (COOH).

2-Exo-bromonorbornane-1-carbonyl chloride:[61]

Thionyl chloride (20 cm^3) was added to 2-exo-bromonorbornane-1-carboxylic acid (19.5 g, 0.09 mol) and the mixture was heated under reflux for 4 h. The mixture was allowed to cool to room temperature, excess thionyl chloride was evaporated off at reduced pressure and the residue distilled at 92 - 93 °C / 3 mm (lit.[61] 122 - 126 °C / 9 mm)

to afford the carbonyl chloride (19.5 g, 92.4 %) as a white solid, m/z 204 (4.0 %), 203 (45.6 %), 202 (3.6 %), 210 (43.5 %), 175 (31.5 %), 173 (36.3 %), 157 (19.5 %), δ_C ($CDCl_3$) 28.8 (C-5), 33.1 (C-6), 36.8 (C-4), 37.8 (C-7), 43.4 (C-3), 52.1 (C-2), 68.43 (C-1).

2-Exo-bromonorbornane-1-carboxamide (37):[61]

2-Exo-bromonorbornane-1-carbonyl chloride (18 g, 0.08 mol) in anhydrous ether (350 cm^3) was cooled in ice and the solution was saturated with gaseous ammonia. The solvent was evaporated off to give a solid. Extraction with hot toluene (3 × 50 cm^3) and cooling gave the carboxamide (15.8 g, 95.5 %), m.p. 174 - 175 °C (lit.[61] 173 - 174 °C), m/z 219 and 217 (M^+, 0.2 and 0.1 %), 138 (91.5 %), 93 (15.3 %), 72 (100 %), δ_C ($CDCl_3$) 29.4 (C-5), 32.7 (C-6), 37.1 (C-4), 37.3 (C-7), 44.0 (C-3), 54.2 (C-2), 59.7 (C-1).

Norbornane-1-carboxamide:[61]

Zinc dust (31 g, 0.47 mol) was added to 2-exo-bromonorbornane-1-carboxamide (15.3 g, 0.07 mol) in acetic acid (180 cm^3) in portions during 30 min with stirring at room temperature and the mixture stirred for a further 42 h.

Water (500 cm^3) was added and the mixture allowed to stand for 4 h. Extraction of the suspension with ether (4 × 200 cm^3) and evaporation of the solvent gave a solid which on recrystallization from water afforded the carboxamide (6.8 g, 69.7 %), m.p. 229 - 230 °C (lit.[61] 235 - 236 °C), m/z 139 (M^+, 100 %), 110 (26.4 %), 95 (13.8 %), 67 (32.0 %), 54 (10.2 %), δ_C ($CDCl_3$) 30.2 (C-3,5), 33.7 (C-2,6), 37.6 (C-4), 41.9 (C-7), 53.4 (C-1), 164.9 ($CONH_2$).

Norbornane-1-carboxylic acid (35):[61]

Norbornane-1-carboxamide (6 g, 0.04 mol) in aqueous potassium hydroxide (20 %, 30 cm^3), was heated under reflux for 42 h. The mixture was allowed to cool and acidified with concentrated hydrochloric acid, to give a precipitate which was filtered, washed with little cold water and dried. Sublimation at 60 °C / 4 mm (lit.[62] 80 °C / 10 mm) gave the acid (4.2 g, 64.7 %), m.p. 107 - 109 °C (lit.[61] 111 - 112 °C).

2-Exo-bromonorbornane-1-carboxylic acid (10 g, 0.05 mol) was dissolved in an ice-cold solution of potassium hydroxide (6 g, 0.11 mol) in water (100 cm^3) and the cold solution was hydrogenated in the presence of 5 % palladium on charcoal catalyst (0.1 g) at 3 atm pressure for one hour. The catalyst was removed by filtration and the filtrate

acidified with concentrated hydrochloric acid to give a precipitate which was filtered, washed with water, and dried. Recrystallization from pentane afforded the acid (5 g, 72 %), m.p. 103 °C, (lit.[81] 111 - 112 °C), m/z 140 (M^+, 38 %), 111 (96.3 %), 112 (26.4 %), 95 (74.1 %), 67 (100 %), 54 (38 %), δ_C ($CDCl_3$) 30.0 (C-3,5), 33.0 (C-2,6), 37.9 (C-4), 42.4 (C-7), 52.2 (C-1), 183.9 (COOH), δ_H ($CDCl_3$) 1.3 - 2.0 (m, 10H), 2.3 (s, 1H, C-4), 10.4 (s, COOH).

Norbornan-1-ol (29)

Hydrogen peroxide (6.24 cm^3, 30 % w/v) was added dropwise to a stirred solution of norbornane-1-carboxylic acid (5 g, 0.04 mol) in concentrated sulphuric acid (50 cm^3) cooled to -10 °C, at such a rate that the temperature was maintained below 0 °C. The mixture was stirred for a further 5 h at -10 °C and then left in the refrigerator for 60 h. The cooled mixture was poured on to crushed ice (150 g) and then stirred in an ice-water bath for 5 h. The mixture was extracted with ether (3 × 150 cm^3) and the combined extracts washed with sodium bicarbonate solution (10 %, 2 × 30 cm^3), water (2 × 20 cm^3) and dried ($MgSO_4$). Evaporation of the ether gave a white solid (2.6 g) which was recrystallised from hexane and dried at 35 °C over $CaCl_2$ to afford the alcohol (29) (2.2 g, 55 %) as colourless plates, m.p. 150 °C (lit.[28] 152 - 154 °C) with sublimation

at 80 - 88 °C, δ_H (CCl_4) 3.1 (s, 1H, OH), 1.38 - 2.0 (br.m, norbornyl), m/z 112 (M^+, 4.2 %), 111 (2.2 %), 83 (100 %), 70 (30.5 %), 54 (16.7 %), ν_{max} 3300 - 3240 (OH), 2960, 2880 , 1455, 1315, 1260, 1220, 1135, 1090, 920 cm^{-1}, δ_C ($CDCl_3$)$^{a)}$ 83.0 (C-1), 43.9 (C-7), 35.4 (C-2,6), 34.8 (C-4), 30.3 (C-3,5).

3.2 Preparations and attempted preparations of phosphorus(III) esters, phosphates and phosphonates

Trinorborn-1-yl phosphite (40):

Phosphorus trichloride (2.04 g, 0.015 mol) in anhydrous light petroleum (50 cm^3) was added dropwise to a stirred solution of norbornan-1-ol (5.27 g, 0.047 mol) and *N,N*-dimethylaniline (5.41 g, 0.045 mol) in anhydrous light petroleum (100 cm^3), cooled in ice and under dried nitrogen. The mixture was then left stirring at room temperature for 60 h. The precipitate was filtered off and washed with light petroleum and the solvent evaporated from the combined filtrate and washings to give a solid which on recrystallization from anhydrous acetonitrile afforded the phosphite (40) (3.5 g, 64.8 %) as a white solid, m.p. 183 - 184 °C (sealed tube), m/z 364 (M^+, 4.4 %), 253 (51.6 %), 95 (100 %), δ_H ($CDCl_3$) 0.96 - 2.45 (m), δ_P ($CDCl_3$) 141.4, δ_C ($CDCl_3$) 86.1 (d, $^2J_{P-C}$ 6.1 Hz, C-1), 43.0 (d, $^3J_{P-C}$ 7.9 Hz, C-7), 35.1 (d, $^3J_{P-C}$ 6.7 Hz, C-2,6), 33.6 (C-4), 30.0 (C-3,5), ν_{max} 2960, 2880, 1455, 1310, 1085 cm^{-1}.

Tris(2,2-diethylbutyl) phosphite (39):

Phosphorus trichloride (0.98 g, 0.007 mol) in anhydrous light petroleum (40 cm^3) was added dropwise to a stirred solution of 2,2-diethylbutan-1-ol (3.04 g, 0.023 mol) and *N,N*-dimethylaniline (2.6 g, 0.021 mol) in anhydrous light petroleum (100 cm^3), cooled in ice and under dried nitrogen. The mixture was allowed to attain room temperature and stirred for 72 h. The precipitate was filtered off and washed with petroleum and the solvent was evaporated from the combined filtrate and washings at reduced pressure. The residue was distilled at 134 - 138 °C / 0.06 mm to give the phosphite (39) (2.27 g, 76 %) as a clear oil, δ_P ($CDCl_3$) 139.7, δ_H ($CDCl_3$) 0.8 (dist.t, 21H, CH_3), 1.06 - 1.47 (m, 18H, $-CCH_2-C$), 3.47 (d, 6H, $^3J_{H-P}$ 6 Hz, CH_2OP), δ_C ($CDCl_3$) 7.4 (CH_3), 25.2 (CH_2), 39.2 (d, $^3J_{C-P}$ 6.1 Hz, $\underline{C}CH_2OP$), 64.7 (d, $^2J_{C-P}$ 9.1 Hz, CH_2OP), ν_{max} 2970, 1465, 1265, 1030, 1010 cm^{-1}.

Trinorborn-1-yl phosphate (41):

t-Butyl hydroperoxide (70 %, 0.12 cm^3) was added to a stirred solution of trinorborn-1-yl phosphite (0.254 g, 0.0007 mol) in anhydrous 1,4-dioxane and the mixture stirred for 1.5 h. The solvent was evaporated in *vacuo* to give the

phosphate (41) (0.26 g, 98 %) as a white solid, m.p. 220 - 221 °C (sealed tube), δ_P ($CDCl_3$) -10.22, m/z 380 (M^+, 16.9 %), 351 (100 %), 287 (16.3 %), 257 (38.5 %) 159 (10.9 %), 95 (64.9 %), 67 (43.2 %), 54 (31.7 %), δ_H ($CDCl_3$) 1.7 - 2.0 (m), δ_C ($CDCl_3$) 89.2 (d, $^2J_{P-C}$ 7.3 Hz, C-1), 42.1 (d, $^3J_{P-C}$ 4.9 Hz, C-7), 33.6 (d, $^3J_{P-C}$ 7.9 Hz, C-2,6), 33.6 (C-4), 29.8 (C-3,5), ν_{max} 2980, 2880, 1455, 1310, 1280, 1085, 1015, 990, 940 cm^{-1}.

Atempted preparations of tris(2,2,2-triphenylethyl) phosphite (42):

Phosphorous trichloride (0.45 g, 0.003 mol) in anhydrous benzene was added dropwise to a stirred solution of 2,2,2-triphenylethanol (2.86 g, 0.01 mol) and *N,N*-dimethylaniline (1.26 g, 0.01 mol) in benzene cooled in ice. The mixture was allowed to attain room temperature after the addition and left stirring for three days. The precipitate that formed was filtered off, washed with benzene and the solvent evaporated off under reduced pressure from the combined filtrate and washings to give a gummy solid product (2.9 g, 98 %), ^{31}P n.m.r. ($CDCl_3$) of the crude solid showed the presence of the tris(2,2,2-triphenylethyl) phosphite (δ 138.7, *ca.* 42 mole %) and bis(2,2,2-triphenylethyl) phosphite (43) (δ 6.71, $^1J_{P-H}$ 717.5 Hz, *ca.* 58 mole %).

Attempts to distil the mixture at reduced pressure resulted in decomposition to give α-phenylstilbene δ_H ($CDCl_3$) 7.26 [s, 10H, $(C_6H_5)_2C$], 7.06 [s, 5H, $C(C_6H_5)$], 6.95 (s, 1H, =CH).

Phosphorus trichloride (1.92 g, 0.014 mol) in anhydrous benzene was added dropwise to a stirred solution of 2,2,2-triphenylethanol (11.8 g, 0.042 mol) and *N,N*-dimethyl aniline (5.08 g, 0.042 mol) in benzene cooled in ice. The reaction was allowed to warm to room temperature after the addition and then left stirring for five days. Continuation of the procedure as in above experiment afforded a gummy solid. ^{31}P n.m.r. ($CDCl_3$) showed the presence of bis(2,2,2-triphenylethyl) phosphite (δ 6.7, $^1J_{P-H}$ 717.5 Hz, *ca.* 76 mole %) and bis(2,2,2-triphenylethyl) chlorophosphite (δ 164.7, *ca.* 24 mole %).

<u>Reaction of 2,2,2-triphenylethanol with phosphorus trichloride:</u>

Phosphorus trichloride (0.126 g, 0.001 mol) in anhydrous deuterochloroform (0.3 cm^3) was added to 2,2,2-triphenylethanol (0.251 g, 0.001 mol) in deuterochloroform (0.3 cm^3) in a ^1H n.m.r tube and the extent of the reaction was followed at suitable intervals by comparing the decreasing signal for the methylene protons in 2,2,2-

triphenylethanol (δ_H 4.6) to the increasing signal for the methylene protons in 2,2,2-triphenylethyl dichlorophosphite (5.1. d, $^3J_{P-H}$ 7.2 Hz) as it was formed. The following results were obtained:

	Approx. composition (mole %)		
Reaction time	ROH	$ROPCl_2$	$(RO)_2P(O)H$
5 min	52	48	
17 min	42	58	
60 min	18	73	9 (δ_H 4.8, d AB, CH_2O-P)
2.6 h		86	14

R = $(C_6H_5)_3CCH_2-$

After 3 h of reaction time, an additional quantity of 2,2,2-triphenylethanol (0.251 g, 0.001 mol) was added to the reaction mixture and the extent of the further reaction was monitored by comparing the decreasing signal for the methylene protons in 2,2,2-triphenyl dichlorophosphite to the increasing signal for the methylene protons in the bis(2,2,2-triphenylethyl) phosphite which was formed. The following results were obtained:

Reaction time	Approx. composition (mole %) ROPCl$_2$	(RO)$_2$P(O)H
10 min	85	15
45 min	71	29
24 h	53	47
^{31}P n.m.r 6 wk	34 (δ_P 177.1)	66 (δ_P 6.7, $^1J_{P-H}$ 725.7 Hz)

R = $(C_6H_5)_2CCH_2$-

Attempted preparation of 2,2,2-triphenylethyl dichlorophosphite (44):

2,2,2-Triphenylethanol (1 g, 0.004 mol) and *N,N*-dimethylaniline (0.55 g, 0.004 mol) in anhydrous ether were added to a stirred solution of phosphorus trichloride (0.75 g, 0.005 mol) in anhydrous ether at room temperature and the reaction left stirring for 24 h. The precipitate that formed was filtered off and washed with ether and the solvent was evaporated from the combined filtrate and washings to give a white gummy solid. ^{31}P n.m.r. ($CDCl_3$) of the crude solid showed the presence of the dichlorophosphite (51) (δ 177.2, *ca.* 67 mole %) and bis(2,2,2-triphenylethyl) phosphite (δ 6.7, *ca.* 33 mol %).

Attempted preparation of 2,2,2-triphenylethyl diphenylphosphinite (47):

Chlorodiphenylphosphine (1.16 g, 0.007 mol) in anhydrous ether (20 cm^3) was added dropwise to a stirred solution of 2,2,2-triphenylethanol (2.0 g, 0.007 mol) and triethylamine (0.74 g, 0.007 mol) in anhydrous ether (60 cm^3) at room temperature and under nitrogen. The reaction was left stirring for three days. The precipitate that formed was filtered off and washed with ether and the solvent evaporated off at reduced pressure from the combined filtrate and washings to give a gummy solid (3.23 g). Recrystallization from anhydrous benzene afforded 2,2,2-triphenylethyl diphenylphosphinate (47), (0.66 g, 19 %), m.p. 140 - 142 °C (Found C, 81.2; H, 5.8 %. $C_{32}H_{27}O_2P$ requires C, 81.0; H, 5.7 %), δ_P ($CDCl_3$) 32.8, δ_C ($CDCl_3$) 144.8 - 126.6 (Ar), 70.0 (d, $^2J_{P-C}$ 6.1 Hz, $CH_2OP(O)$), 57.6 [d, $^2J_{P-C}$ 8.5 Hz, $(C_6H_5)_3\underline{C}$-], δ_H ($CDCl_3$) 7.24 - 7.56 (m, Ar), 4.97 (d, $^2J_{P-H}$ 3.4 Hz, CH_2OP), m/z 256 [84.1 %, $(C_6H_5)_2C{=}CHC_6H_5^{+\cdot}$], 255 (14.3 %), 243 [100 %, $(C_6H_5)_3C^+$], 217 [1.4 %, $OP(O)(C_6H_5)_2^+$], 201 [9.6 %, $P(O)(C_6H_5)_2^+$].

The ^{31}P n.m.r. spectrum of the residue in the mother liquor showed the presence of a mixture of compounds at δ 30.5 (*ca.* 23 mole %), δ 31.7 (*ca.* 64 mole %) and δ 35.2 (*ca.* 13 mole %).

The experiment was repeated with a different batch of anhydrous ether in which a positive result was obtained for peroxide test. The ^{31}P n.m.r. spectrum of the crude product showed the presence of 2,2,2-triphenylethyl diphenyl phosphinate (δ 32.1, *ca.* 38 mole %), 2,2,2-trphenylethyl diphenylphosphinite (δ 116.1, *ca.* 6 mole %), and unidentified compounds (δ 31.0, *ca.* 37 mole %, δ 28.3, *ca.* 14 mole % and δ 21.2, *ca.* 5 mole %).

2,2,2-Triphenylethyl diphenylphosphinite (47):

Chlorodiphenylphosphine (2.46 g, 0.01 mol) in benzene-ligroin mixture (2:1, 20 cm^3) was added to a stirred solution of 2,2,2-triphenylethanol (3.06 g, 0.01 mol) and triethylamine (1.13 g, 0.01 mol) in anhydrous benzene-ligroin mixture (2:1, 50 cm^3) cooled in ice and under dried nitrogen. The reaction was left stirring in ice for a further 3 h after the addition and then left stirring for 3 days at room temperature. The precipitate that formed was filtered off and washed with benzene-ligroin and the solvent was evaporated from the combined filtrate and washings to give a gummy solid (5.4 g, 105 %). ^{31}P n.m.r. ($CDCl_3$) of the crude solid showed the presence of the diphenylphosphinite (δ 116.0, *ca.* 47 mole %), 2,2,2-triphenylethyl diphenylphosphinate (δ 32.2, *ca.* 24 mole %), and unidentified compounds(δ 31.3, *ca.* 20 mole % and δ 21.4,

ca. 9 mole %). Trituration of the crude solid with benzene afforded the **phosphinite** (47) (0.45 g, 8.8 %) as a white solid, m.p. 131 - 133 °C, δ_P ($CDCl_3$) 116.1, δ_H ($CDCl_3$) 7.22 (s, Ar), 4.8 (d, $^3J_{P-H}$ 6 Hz, CH_2OP), δ_C ($CDCl_3$) 145.5 - 126.4 (Ar), 75.6 (d, $^2J_{P-C}$ 11 Hz, CH_2OP), 58.6 (d, $^3J_{P-C}$ 9.8 Hz, $-C-CH_2OP$), m/z 257 [46.5 %, $(C_6H_5)_2CCH_2^+$], 256 (38.2 %), 255 (7.3 %), 243 [34.9 %, $(C_6H_5)_2C^+$], 202 [23.3 %, $HP(O)(C_6H_5)_2^+$], 201 [42.1 %, $OP(C_6H_5)_2^+$], 185 [7.5 %, $P(C_6H_5)_2^+$], 180 [100 %, $(C_6H_5)_2CCH_2^+$], ν_{max} (KBr disc) 1595 (C=C), 1490 (C=C), 1445 (P-Ar), 1430, 1090, 1050, 795, 705 cm^{-1}.

Attempted preparation of bis(2,2,2-triphenylethyl) phenylphosphonite (48):

Dichlorophenylphosphine (0.66 g, 0.004 mol) in anhydrous benzene-ligroin mixture (2:1, 10 cm^3) was added dropwise to a stirred solution of 2,2,2-triphenylethanol (2.02 g, 0.007 mol) and triethylamine (0.74 g, 0.007 mol) in anhydrous benzene-ligroin (55 cm^3), cooled in ice and under dried nitrogen. The reaction was left stirring for a further 3 h in ice after the addition and then left stirring at room temperature for 3 days. The precipitate that formed was filtered off and washed with benzene-ligroin mixture and the solvent was evaporated at reduced pressure from the combined filtrate and washings to give an oily product

(2.97 g.); ^{31}P n.m.r. ($CDCl_3$) of the oil showed the presence of unidentified compounds, (δ 26.6, *ca.* 3 mole %; δ 26.1, *ca.* 3 mole %; δ 20.0, *ca.* 32 mole %; δ 17.0, *ca.* 39 mole %; δ 9.9, *ca.* 13 mole % and δ 9.7, *ca.* 9 mole %).

Dineopentyl 1-methylvinyl phosphate (49):

Chloroacetone (1.65 g, 0.018 mol) was added dropwise to stirred trineopentyl phosphite (4.35 g, 0.015 mol) at 70 °C and the reaction maintained between 65 - 75 °C for 24 h. The mixture was allowed to cool and then distilled at 72 - 76 °C / 0.1 mm to give the phosphate (49) (3.65 g, 88 %) as a clear oil, δ_P ($CDCl_3$) -6.8, δ_H ($CDCl_3$) 0.96 [s, 18H, $(CH_3)_3C$], 1.94 (s, 3H, $CH_3C=$), 3.73 (d, 4H, $^3J_{H-P}$ 5 Hz, CH_2OP), 4.63 (d, 2H, $=CH_2$), δ_C ($CDCl_3$) 20.7 (d, $^3J_{C-P}$ 5.5 Hz, $CH_3-C=$), 26.1 [$(CH_3)_3C$], 32.2 (d, $^3J_{C-P}$ 7.9 Hz, CCH_2OP), 77.4 (d, $^2J_{C-P}$ 7.3 Hz, CH_2OP), 98.2 (d, $^3J_{C-P}$ 4.9 Hz, $=CH_2$), 152.3 (d, $^2J_{C-P}$ 8.5 Hz, P-O-C=), ν_{max} 2965, 1665 (C=C), 1485, 1285, 1030 cm^{-1}, m/z 278 (7.8 %), 208 (17.6 %), 193 (37.4 %), 152 (73.4 %), 151 (6.1 %), 138 (100 %).

Dineopentyl acetonylphosphonate (50)

Trineopentyl phosphite (5.09 g, 0.017 mol) in anhydrous toluene (20 cm^3) was added to iodoacetone (3.85 g, 0.021 mol) in anhydrous toluene (10 cm^3) and the mixture heated under reflux for 48 h. The reaction mixture was cooled, the solvent and neopentyl iodide were evaporated in *vacuo* and the residue distilled at 108 - 110 °C / 0.3 mm to give the phosphonate (50) (2.71 g, 56 %) as a clear oil, δ_P ($CDCl_3$) 19.45, δ_H ($CDCl_3$) 0.95 [s, 18H, $(CH_3)_3C$], 2.34 (s, 3H, $COCH_3$), 3.1 (d, 2H, $^2J_{P-H}$ 22 Hz, PCH_2), 3.72 (d, 4H, $^3J_{H-P}$ 5 Hz, CH_2OP), δ_C ($CDCl_3$) 26.1 [$(CH_3)_3$-], 31.3 ($COCH_3$), 32.2 (d, $^3J_{C-P}$ 7.3 Hz, CCH_2OP), 43.0 (d, $^1J_{C-P}$ 127.6 Hz, PCH_2), 75.8 (d, $^2J_{C-P}$ 7.3 Hz, CH_2OP), 199.6 (d, $^2J_{C-P}$ 6.1 Hz, C=O), ν_{max} 2960, 1710 (C=O), 1475, 1255, 1010 cm^{-1}.

3.3 Preparations of miscellaneous compounds

Iodoacetone:[63]

Potassium iodide (38.0 g, 0.23 mol) in water (40 cm^3) was added to freshly distilled chloroacetone (20.0 g, 0.22 mol) and methanol was added slowly until a homogenous solution was obtained. The mixture was left standing for 24 h at room temperature. The reddish brown oily layer that formed was separated from the aqueous layer, washed with water (2 × 20 cm^3), dried ($CaSO_4$) and distilled at 96 °C / 25 mm (lit.[63] b.p. 58.4 °C / 11 mm) to afford iodoacetone as a light brown oil (16.5 g, 41.3 %), δ_H ($CDCl_3$) 2.4 (s, 3H, CH_3), 3.8 (s, 2H, CH_2I).

α-Bromo-p-nitroacetophenone:[64]

Bromine (8.0 g, 0.05 mol) was added to a stirred suspension of p-nitroacetophenone in hydrochloric acid (33 %, 14 cm^3) and the mixture stirred for 18 h at room temperature. The suspension was extracted into ether (2 × 70 cm^3) and the ether extract washed with sodium bisulphite (10 %, 20 cm^3), and dried ($MgSO_4$). Evaporation of the solvent and recrystallization from benzene-ligroin mixture afforded the acetophenone (5.6 g, 46 %) as a yellow solid, m.p. 91 - 92 °C (lit.[64] 97 - 98 °C), δ_H ($CDCl_3$) 4.4 (s,

CH_2Br), 8.1 (AA'BB' pattern, Ar), ν_{max} 1705 (C=O), 1600 (C=C), 1515 ($ArNO_2$), 1345 ($ArNO_2$), 1195, 1000, 850, 750 cm^{-1}.

α-Chloro-p-nitroacetophenone:[64]

Sulphuryl chloride (10.0 g, 0.07 mol) was added dropwise to a stirred solution of p-nitroacetophenone (8.25 g, 0.05 mol) in anhydrous chloroform at room temperature and the mixture heated for 6 h between 60 - 70 °C. Chloroform and excess sulphuryl chloride were distilled off at reduced pressure to give a solid residue which was recrystallized from absolute ethanol to afford the acetophenone (6.02 g, 60.4 %) as a brown solid, m.p. 85 °C (lit.[64] 90 °C), δ_H ($CDCl_3$) 4.7 (s, CH_2Cl), 8.1 (AA'BB' pattern, Ar), ν_{max} 1705 (C=O), 1600 (C=C), 1510 ($ArNO_2$), 1345 ($ArNO_2$), 1205, 1005, 850, 775, 750 cm^{-1}.

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3.4 Interaction of trialkyl phosphites with α-haloketones

General method for monitoring the reactions of phosphorus(III) esters with α-haloacetophenones by ^{31}P and ^{1}H n.m.r.

α-Haloacetophenone (1 mol. equiv.) in deuterochloroform was added to a solution of the phosphorus(III) ester (1 mol. equiv.) in deuterochloroform in an n.m.r. tube and the reaction was monitored by ^{31}P n.m.r. (or ^{1}H n.m.r.) spectroscopy at intervals. The total amount of the solvent used was such that the initial concentration of the ester in the mixture was about 20 %. The results of the experiments are shown in Table 11, where KPS = the ketophosphonium salt (Arbuzov intermediate), $(RO)_3PCH_2COC_6H_4Y$ X , VPS = the vinyloxyphosphonium salt (Perkow intermediate), $(RO)_3POC(C_6H_4Y)=CH_2$ X , KP = the ketophosphonate, $(RO)_2P(O)CH_2COC_6H_4Y$, VP = the vinyl phosphate, $(RO)_2P(O)C(C_6H_4Y)=CH_2$, and A = additional major side product(s) obtained.

Table 11

Reactions of phosphorus(III) esters, $(RO)_3P$, with α-haloacetophenone $XCH_2COC_6H_4Y$-p, and haloacetones, ZCH_2COCH_3.

				Products δ_P ($CDCl_3$) (Approx. mole %)[a]				
R	X	Y	Reaction times (h)[b]	$(RO)_3P$	KPS	VPS	KP	VP
$(CH_3)_3CCH_2$-								
		(Z = Cl)						-6.8
		(Z = Cl)						-6.8
		(Z = I)					19.4	-6.8
	Br	Br				39.8	18.9	
			7.4			(10)	(21)	
	Br	Br			137.3	40.2	18.3	
			7.4		(16)	(4)	(60)	
$(CH_3CH_2)_3CCH_2$-								
	Br	H			139.9	40.6	19.7	
			0.3		(73)	(11)	-	
			0.6		(49)	(20)	(3)	
			1.1		(26)	(23)	(8)	
			3.6			(5)	(32)	
			17.1				(36)	
	Cl	H			139.6			-6.0
			0.3		(70)			(30)
			20.0					(100)

Table 11 continued

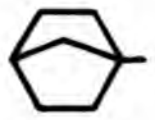
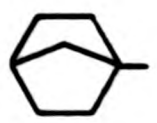
R	X	Y	Reaction times (h)[b]	Products δ_P ($CDCl_3$) (Approx. mole %)[a] $(RO)_3P$	KPS	VPS	A	$(RO)_3PO$	$(RO)_2P(O)H$
	Br	H		141.6	27.1				
			0.3	(89)	(11)				
			1.0	(67)	(33)				
			1.3	(64)	(36)				
			1.9	(50)	(50)				
			2.9	(41)	(59)				
			21.0	(6)	(94)				
	Cl	H		No Reaction					
	Cl	H		26.7			41.9, -14.3	-10.4	-0.2
			65.0 (at 69 °C)	(31)			(30) (3)	(31)	(5)
	(Z = Cl)			No Reaction					
	(Z = Cl)			26.4	-16.9		116.0, 29.2	-10.4	-0.4
			71.5 (at 69 °C)	(12)	(8)		(21) (15)	(15)	(11)
							23.5, -4.4		
							(14) (4)		
	Br	Br		26.3					

Table 11 continued

R	X	Y	Reaction times (h)[b]	Products δ_P ($CDCl_3$) (Approx. mole %)[a] $(RO)_3P$	KPS	VPS	A	$(RO)_3PO$
	Cl	NO_2		141.9		-17.0		
			0.3	(89)		(11)		
			0.6	(80)		(20)		
			1.3	(55)		(45)		
			23.2	(8)		(92)		
	Br	NO_2			25.2	-16.9	11.2, -10.7	-10.3
			24.0		(12)	(16)	(29) (15)	(28)

[a] Approximate mole ratios calculated from the proton decoupled spectra.

[b] Reactions carried out at room temperature except where specified.

Reaction of trinorborn-1-yl phosphite with α-bromo-p-nitroacetophenone:

α-Bromo-p-nitroacetophenone (0.333 g, 0.0013 mol) and trinorborn-1-yl phosphite (0.488 g, 0.0013 mol) in deuterochloroform (2.5 cm^3) were sealed in an n.m.r. tube and the reaction was monitored at intervals by ^{31}P n.m.r. A mixture of phosphorus-containing compounds was obtained. The spectrum after 24 h showed the presence of trinorborn-1-yloxy(p-nitrophenacyl)phosphonium bromide (65) (δ_P 25.2, t, $^2J_{P-H}$ 17.2 Hz, *ca.* 11.5 mole %), trinorborn-1-yl phosphate (δ_P -10.3, *ca.* 28 mole %), trinorborn-1-yloxy-1-(p-nitrophenyl)vinyloxyphosphonium bromide (64) (δ_P -16.9, *ca.* 16.4 mole %), and two unidentified compounds: (δ_P 11.3, d, J_{P-H} 20.6 Hz, *ca.* 29 mole %; δ_P -10.7, s, *ca.* 15.1 mole %). The ^1H n.m.r. spectrum showed, in addition to the presence of the p-nitrophenacylphosphonium bromide (65) (δ_H 5.4, d, $^2J_{H-P}$ 17.2 Hz, PCH_2) and the vinyloxyphosphonium bromide (64) (δ_H 6.3 and 5.5, m, $=CH_aH_b$), a small unidentified signal at δ_H4.1 and a large signal at δ_H 2.7 due to p-nitroacetophenone. Evaporation of the solvent and trituration of the residue with anhydrous ether afforded a gummy solid which was washed several times with ether by decantation and dried in *vacuo* to give a mixture of compounds (0.411 g,). ^{31}P ($CDCl_3$) showed the presence of the vinyloxyphosphonium bromide (64) (*ca.* 25 mole %), the phenacylphosphonium bromide (65) (*ca.* 16.9 mole %), and

three unidentified compounds: (δ_P -10.7 *ca.* 8.6 mole %; δ_P 11.4, *ca.* 35.6 mole %; δ_P 13.7, *ca.* 13.9 mole %), *V* max 1695 (C=O) 1600 (C=C), 1455, 1515, 1350, 1315, 1265, 1085, 1000, 945, 920, 860 cm^{-1}, m/z (FAB) 592 (6.9 %), 590 (6.3 %), 528 (7.5 %), 381 (23.7 %), 379 (4.9 %), 287 (8.4 %), 95 (100 %).

Evaporation of the solvent from the washings gave trinorbornyl phosphate, δ_P ($CDCl_3$) -10.2, as the only phosphorus-containing compound. The mixture of compounds obtained above (0.145 g) was washed again with ether, dried in *vacuo* and dissolved in deuterochloroform (1.0 cm^3) in a sealed n.m.r. tube. The tube was heated in an oil bath at 149 °C for 24 h. The ^{31}P n.m.r. spectrum of the decomposed mixture showed the presence of dinorborn-1-yl p-nitrophenacylphosphonate (69) (δ_P 12.2, *ca.* 7.5 mole %), trinorborn-1-yl phosphate (δ_P -10.6, *ca.* 60 mole %) and unidentified compound(s): (δ_P 4.7 and δ_P 4.5 of the same intensity, *ca.* 32.5 %).

Reaction of trinorborn-1-yl phosphite with α-chloroacetophenone:

α-Chloroacetophenone (0.0307 g, 0.0002 mol) in deuterochloroform (0.5 cm^3) was added to trinorborn-1-yl phosphite (0.0683 g, 0.0002 mol) in a sealed n.m.r. tube and

the tube heated at 69 °C for 65 h. The ^{1}H n.m.r. spectrum of the solution showed the presence of phenylacetylene (δ 3.1, C≡CH), trinorborn-1-yloxy(phenacyl)phosphonium chloride (58), (δ_H 5.2, d, $^2J_{H-P}$ 18 Hz, PCH_2) and an unidentified signal at δ_H5.7 (d, J 14.4 Hz). The ^{31}P n.m.r. spectrum showed the presence of trinorborn-1-yloxy-(phenacyl)phosphonium chloride (58), (δ_P 26.7, t, $^2J_{P-H}$ 18 Hz, *ca.* 31 mole %), dinorborn-1-yl phosphite (δ_P -0.2, d, $^1J_{P-H}$ 684.3 Hz, *ca.* 5 mole %), trinorborn-1-yl phosphate (δ_P -10.4, *ca.* 31 mole %), and two unidentified compound: (δ_P 41.9, s, *ca.* 30 mole %; δ_P -14.3, s, *ca.* 3 mole %).

Reaction of trinorborn-1-yl phosphite with chloroacetone:

α-Chloroacetone (0.0177 g, 0.0002 mol) was added to trinorborn-1-yl phosphite (0.0699 g, 0.0002 mol) in deuterochloroform (0.5 cm^3) in a sealed n.m.r. tube and the tube heated at 69 °C for 71.5 h. The ^{31}P n.m.r. spectrum of the mixture showed the presence of trinorborn-1-yloxy-1-methylvinyloxyphosphonium chloride (62), (δ_P -16.9, *ca.* 7.8 mole %), trinorborn-1-yl phosphate (δ_P -10.4, *ca.* 15.4 mole %), dinorborn-1-yl phosphite (δ_P -0.4, d, $^1J_{P-H}$ 685.3 Hz, *ca.* 11.3 mole %), trinorborn-1-yloxy(acetonyl) phosphonium chloride (61), (δ_P 26.4, t, $^2J_{P-H}$ 18.5 Hz, *ca.* 11.7 mole %) and four unidentified compounds: (δ_P 116.0, s, *ca.* 20.5 mole %; δ_P 29.2, d, J_{P-H} 24.0 Hz, *ca.* 14.7 mole %;

δ_P 23.5, d, J_{P-H} 24.0 Hz, *ca.* 14 mole %; δ_P -14.4, s, *ca.* 4.3 mole %).

3.5 Reactions of trimethyl phosphite with chloroacetophenones in methanol.

Reaction with α-chloroacetophenone:

α-Chloroacetophenone (0.452 g, 0.0029 mol) in anhydrous methanol (1.0 cm^3, 80 % v/v spectrosol methanol in methanol-d_4) was added to trimethyl phosphite (0.294 g, 0.0024 mol) in anhydrous methanol (1.5 cm^3) in an n.m.r. tube and the reaction was monitored at suitable intervals by ^{31}P n.m.r. The results obtained are shown in Table 12.

With α-chloroacetophenone and pyridine:

α-Chloroacetophenone (0.4353 g, 0.0028 mol) and dried pyridine (0.222 g, 0.0028 mol) in anhydrous methanol (1.0 cm^3, 80 % v/v spectrosol methanol in methanol-d_4) were added to trimethyl phosphite (0.291 g, 0.0023 mol) in anhydrous methanol (1.5 cm^3) in an n.m.r. tube and the reaction was monitored at suitable intervals by ^{31}P n.m.r. The results obtained are shown in Table 12.

Table 12

^{31}P n.m.r. results of the reaction of trimethyl phosphite with α-chloroacetophenones in methanol.

$ClCH_2CO-C_6H_4Y-p$	Reaction Time (min)	Products ^{31}P δ_P (Approx. mole %) R = CH_3 $(RO)_3P$	$(RO)_2P(O)CH_3$	$(RO)_2P(O)C(OH)(CH_2Cl)C_6H_4Y$	$(RO)_2P(O)H$	$(RO)_3PO$	$(RO)_2P(O)OC(C_6H_4Y):CH_2$
Y = H		140.5	34.3	21.8	11.3		-4.8
	2	(72)	(2)	(12)	(2)		(12)
	10	(17)	(5)	(39)	(4)		(35)
	30	(2)	(10)	(45)	(8)		(35)
	60		(8)	(47)	(10)		(35)
	3 h		(10)	(43)	(14)		(34)
Y = H + C_5H_5N		140.4				1.5	-4.9
	4	(89)				(6)	(5)
	8	(71)				15)	(14)
	15	(50)				20)	(30)
	30	(35)				21)	(44)
	3 h	(10)				26)	(64)
Y = NO_2				20.5	11.6	1.6	-4.8
	5			(4)	(28)	(7)	(61)
	55			(4)	(28)	(7)	(61)

With α-chloro-p-nitroacetophenone:

α-Chloro-p-nitroacetophenone (0.4285 g, 0.0021 mol) in anhydrous methanol (1.0 cm^3, 80 % v/v spectrosol methanol in methanol-d_4) was added to trimethyl phosphite (0.22 g, 0.0018 mol) in anhydrous methanol (1.5 cm^3) in an n.m.r. tube and the reaction was monitored at suitable intervals by ^{31}P n.m.r. The results obtained are shown in Table 12.

Reaction of dimethyl α-hydroxy-α-chloromethyl-benzylphosphonate (81) with pyridine:

Pyridine (0.072 g, 0.0009 mol) was added to the phosphonate (81), (0.24 g, 0.00086 mol) in anhydrous methanol and the reaction left at room temperature. The ^{31}P n.m.r. spectrum of the mixture after six days showed no reaction.

Reactions of varying concentrations of trimethyl phosphite with α-chloroacetophenones

With α-chloroacetophenone:

Freshly distilled trimethyl phosphite (Table 13) warmed to 26.5 °C in a thermostatted oil bath was added to four sealed flasks containing α-chloroacetophenone (Table 13) in

anhydrous methanol (85 % v/v spectrosol methanol in methanol-d_4) placed in a thermostatted oil bath at 26.5 °C. The reactions were left in the oil bath for one hour and then cooled below 0 °C. ^{31}P gated decoupling n.m.r. was immediately run on the samples. The results obtained are shown in Tables 14.

With α-chloro-p-chloroacetophenone:

Freshly distilled trimethyl phosphite (Table 13) warmed to 25.7 °C in a thermostatted oil bath was added to two sealed flasks containing α-chloro-p-chloroacetophenone (Table 13) in anhydrous methanol (85 % v/v spectrosol methanol in methanol-d_4) placed in a thermostatted oil bath at 25.7 °C. The reactions were left in the oil bath for one hour and then left at room temperature. ^{31}P gated decoupling n.m.r. was run on the samples after about 18 h, at room temperature. The results obtained are shown in Tables 14.

Table 13

Quantities of reactants used in the reactions of varying concentrations of trimethyl phosphite with α-chloroacetophenones.

$(CH_3O)_3P$: $ClCH_2COC_6H_4Y$ mole ratio	$(CH_3O)_3P$	$ClCH_2COC_6H_4Y$	CH_3OH/CD_3OD
Y = H			
20 : 1	0.489 g, 0.004 mol	0.0305 g, 0.0002 mol	4 cm^3
10 : 1	0.491 g, 0.004 mol	0.0612 g, 0.0004 mol	4 cm^3
5 : 1	0.4772 g, 0.004 mol	0.119 g, 0.0008 mol	4 cm^3
1 : 1	0.4614 g, 0.0037 mol	0.5753 g, 0.0037 mol	4 cm^3
Y = Cl			
20 : 1	0.8705 g, 0.007 mol	0.0646 g, 0.0003 mol	4 cm^3
1 : 1	0.2963 g, 0.0024 mol	0.4516 g, 0.0024 mol	2.5 cm^3

Table 14

^{31}P gated decoupling n.m.r. results of the reactions of α-chloroacetophenones with varying concentrations of trimethyl phosphite (R = CH_3).

$(RO)_3P$: $ClCH_2COC_6H_4Y$ mole ratio	Products δ_P (Approx. mole %)				
	$(RO)_2P(O)CH_3$	$(RO)_2P(O)C(OH)-(CH_2Cl)C_6H_4Y$	$(RO)_2P(O)H$	$(RO)_3P(O)$	$(RO)_2P(O)O-C(C_6H_4Y)=CH_2$
Y = Cl					
1 : 1	34.5 (10)	21.4 (28)	11.5 (21)	1.7 (4)	-4.7 (37)
20 : 1	(46)	(4)	(32)	(5)	(13)
Y = H					
1 : 1	34.4 (12)	21.9 (42)	11.4 (9)	1.8 (2)	-4.7 (35)
5 : 1	(25)	(25)	(26)	(4)	(20)
10 : 1	(25)	(20)	(36)	(2)	(17)
20 : 1	(32)	(8)	(43)	(5)	(12)

Solvent CH_3OH / CD_3OD

3.6 **Reactions of benzoyl chloride with trineopentyl phosphite and trisarborn-1-yl phosphite (40).**

Reaction with trineopentyl phosphite:

Benzoyl chloride (0.364 g, 0.0026 mol) was added to trineopentyl phosphite (0.756 g, 0.0026 mol) in deuterochloroform (2.5 cm^3) in an n.m.r. tube and the reaction was monitored at suitable intervals by ^{31}P n.m.r. A mixture of phosphorus-containing compounds was obtained. The results are as follows:

	Approx. composition (mole %)						
Products ^{31}P	6 min	11 min	15 min	20 min	53 min	20.2 h	3 months
138.2 $[(CH_3)_3CCH_2O]_3P$	83	78	77	79	69	27	-
27.4 (Unidentified)	7	3	1	-	-	-	-
16.4 (Unidentified)	1	6	9	8	11	16	24
12.2 (Unidentified)	-	-	-	-	-	2	4
4.7 (Unidentified)	-	-	-	-	-	1	2
-1.2 $[(CH_3)_3CCH_2O]_3PO$	10	13	14	13	16	24	31
-1.8 $[(CH_3)_3CCH_2O]_2P(O)C(O)C_6H_5$	-	-	1	1	4	30	39

(lit.[38] $(C_2H_5O)_2P(O)COC_6H_5$ δ_P -1.8)

The ^{13}C n.m.r. spectrum of the mixture showed, the presence of a P–C bond at δ_C 53.7 (d, $^1J_{P-C}$ 160.5 Hz), and ^1H n.m.r. showed the presence of two doublets at δ_H 5.2 (J 13.2 Hz)

and δ_H 5.7 (J 7.2 Hz), which cannot be conclusively assigned.

Reaction with trinorborn-1-yl phosphite:

Benzoyl chloride (0.18 g, 0.0013 mol) was added to trinorborn-1-yl phosphite (0.467 g, 0.0013 mol) in deuterochloroform (2.5 cm^3) in an n.m.r. tube and the reaction was monitored at suitable intervals by ^{31}P n.m.r. A mixture of phosphorus-containing compounds was obtained. The results are as follows:

		Approx. composition (mole %)		
Products	^{31}P	2 h	21.2 h	3 months
	141.5 $(C_7H_{11}O)_3P$	no reaction	88	-
	52.8 (Unidentified)		-	2
	31.4 (Unidentified)		-	11
	20.1 (Unidentified)		-	2
	15.3 (Unidentified)		2	5
	12.8 (Unidentified)		2	18
	-10.6 $(C_7H_{11}O)_3PO$		8	55
	-14.13 (Unidentified)		-	7

Chloroform was evaporated at reduced pressure from the final reaction mixture and trituration of the oily residue with anhydrous ether afforded a solid which was washed several

times with anhydrous ether by decantation and dried in *vacuo* (0.134 g). ^{31}P n.m.r. ($CDCl_3$) showed a mixture of unidentified compounds: (δ_P 31.7 *ca.* 15 mole %; δ_P 20.4, *ca.* 62 mole %; δ_P 15.7, *ca.* 7 mole %; δ_P -14.2, *ca.* 16 mole %). The ^{13}C n.m.r. spectrum showed the presence of a P-C bond at δ 55.1 (d, $^1J_{P-C}$ 142.8 Hz) and two carbonyl groups at δ_C 194.0 and 194.2.

3.7 Isolation of quasiphosphonium salts.

Trinorborn-1-yloxy(phenacyl)phosphonium bromide (57):

Bromoacetophenone (0.24 g, 0.0012 mol) and trinorborn-1-yl phosphite (0.437 g, 0.0012 mol) in deuterochloroform (2.5 cm^3) were sealed in a ^{31}P n.m.r. tube and the reaction was monitored at intervals by ^{31}P n.m.r. for 24 h. The chloroform was evaporated at reduced pressure and trituration with anhydrous ether gave a solid which was washed several times with anhydrous ether by decantation and dried in *vacuo* to afford the phosphonium bromide (57) (0.275 g, 40.6 %), m.p. 170-172 °C, m/z (FAB) 483 (P^+ ion, 100 %), 389 (16.0 %), 364 (1.2 %), 253 (8.9 %), 95 (61.6 %), δ_P ($CDCl_3$) 26.7, δ_H ($CDCl_3$ 1.38-2.2 (m, 33H, norbornyl), 5.22 (d, 2H, $^2J_{P-H}$ 18.1 Hz, PCH_2), 7.58 (m, 3H, Ar), 8.4 (m, 2H, Ar), δ_C ($CDCl_3$ 190.2 (d, $^2J_{P-C}$ 7.9 Hz, C=O), 135.7 (d, $^3J_{P-C}$ 7.3 Hz, ArC-1), 134.6 (ArC-4), 130.1 (ArC-2,6), 129.1 (ArC-3,5), 98.0 (d, $^2J_{C-P}$ 12.2 Hz, norbornyl C-1), 42.4 (d, $^3J_{C-P}$ 3.7 Hz, norbornyl C-7) 40.6 (d, $^1J_{C-P}$ 134.9 Hz, PCH_2), 33.8 (d, $^3J_{C-P}$ 3.1, norbornyl C-2,6), 32.8 (norbornyl C-4), 29.6 (norbornyl C-3,5), ν_{max} 2960, 1680 (C=O), 1595, 1450, 1090 - 1070 (br, C-O-P) cm^{-1}.

Bromoacetophenone (0.5759 g, 0.0029 mol) and trinorborn-1-yl phosphite (0.9126 g, 0.0025 mol) in anhydrous ether (10 cm^3) were left standing at ambient temperature for eleven

days. The white crystals which separated out were washed several times with anhydrous ether by decantation and dried in *vacuo* to afford the phosphonium bromide (57) (0.9477 g, 67.1 %), m.p. 177-178 °C, (Found: C, 62.9; H, 7.2; $C_{29}H_{40}BrO_4P$ requires C, 61.8; H, 7.1 %).

Trinorborn-1-yloxy(p-bromophenacyl)phosphonium bromide (66):

Trinorborn-1-yl phosphite (0.1285 g, 0.0003 mol) and α-bromo-p-bromoacetophenone (0.6 cm^3) were sealed in an n.m.r. tube and the reaction was monitored at intervals by ^1H n.m.r. for 24 h. Work up as in the above experiment afforded the phosphonium bromide (66) (0.13 g, 57.3 %) as a brown solid, m.p. 172-173 °C, δ_P ($CDCl_3$) 26.3 (t, $^2J_{P-H}$ 18 Hz), δ_C ($CDCl_3$) 134.3 (d, $^2J_{C-P}$ 8.5 Hz, ArC-1), 132.4 (ArC-3,5), 131.8 (ArC-2,6), 130.3 (ArC-4), 98.0 (d, $^2J_{C-P}$ 12.2 Hz, norbornyl C-1), 42.4 (d, $^2J_{C-P}$ 3.7 Hz, norbornyl C-7) 40.7 (d, $^1J_{C-P}$ 136.1 Hz, PCH_2), 33.8 (d, $^3J_{C-P}$ 3.0 Hz, norbornyl C-2,6), 32.8 (norbornyl C-4), 29.6 (norbornyl C-3,5), ν_{max} 2985, 2880, 1685, 1580, 1315, 1080 cm^{-1}, m/z (FAB) 564 (P^+ ion, 18.4 %), 562 (P^+ ion, 18.4 %), 563 (54.7 %), 561 (54.6 %), 379 (2.0 %), 253 (6.2 %), 95 (100 %), δ_H ($CDCl_3$) 1.2 - 2.2 (norbornyl), 5.15 (d, $^2J_{H-P}$ 18.6 Hz, PCH_2).

Norbornyl-1-oxy-1-(p-nitrophenyl)vinyloxyphosphonium chloride (63):

α-Chloro-p-nitroacetophenone (0.2733 g, 0.0014 mol) and trinorborn-1-yl phosphite (0.4818 g, 0.0013 mol) in deuterochloroform (2.5 cm^3) were sealed in a ^{31}P n.m.r. tube and the reaction was monitored at intervals by ^{31}P n.m.r. for 24 h. Work up as in the above experiment afforded the vinyloxyphosphonium chloride (63) (0.529 g, 71 %), m.p. 120-123 °C, δ_P ($CDCl_3$) -17.1, δ_C ($CDCl_3$) 150.4 (d, $^2J_{C-P}$ 9.8 Hz, POC=), 148.8 (ArC-NO_2), 137.5 (d, $^3J_{C-P}$ 7.9 Hz, ArC-1), 127.0 (ArC-2,6), 124.5 (ArC-3,5), 105.4 (=CH_2), 100.5 (d, $^2J_{C-P}$ 11.6 Hz, norbornyl C-1), 42.3 (d, $^3J_{C-P}$ 4.3 Hz, norbornyl C-7), 33.5 (d, $^3J_{C-P}$ 3.1 Hz, norbornyl C-2,6), 32.7 (norbornyl C-4), 29.5 (norbornyl C-3,5), δ_H ($CDCl_3$) 5.48 (1H, dd, POC=CH_A, $^1J_{HA-HB}$ 5.6 Hz, $^4J_{HA-P}$ 1.7 Hz), 6.37 (1H, dd, POC=CH_B, $^1J_{HA-HB}$ 5.6 Hz, $^4J_{HB-P}$ 2.6 Hz), 7.86-8.4 (q, AA'BB', 4H, Ar), m/z (FAB) 528 (P^+ ion, 11.2 %), 381 (47.5 %), 287 (16.2 %), 95 (100 %), ν_{max} 2985, 1640, 1610, 1525, 1460, 1355, 1100, 1045, 1005 cm^{-1}.

α-Chloro-p-nitroacetophenone (0.2303 g, 0.0011 mol) and trinorborn-1-yl phosphite (0.3071 g, 0.0008 mol) in anhydrous ether (10 cm^3) were left in the refrigerator for 4 weeks. The yellowish brown crystals which separated out were washed several times with anhydrous ether by decantation and dried in *vacuo* to afford the

vinyloxyphosphonium chloride (63) (0.384 g, 81 %) as a yellowish crystals, m.p. 121 - 123 °C.

Trinorborn-1-yloxy(methyl)phosphonium iodide (75):

Trinorborn-1-yl phosphite (0.3426 g, 0.0009 mol) and methyl iodide (0.16 g, 0.0011 mol) mixed in deuterochloroform (1.0 cm^3) were left stirring at room temperature for 24 h. Evaporation of the solvent at reduced pressure and trituration of the residue with anhydrous ether afforded a yellow solid which was washed several times with ether by decantation to afford the phosphonium iodide (75) (0.417 g, 87.6 %), m.p. 140-145 °C, δ_H ($CDCl_3$) 2.5 (d, $^2J_{H-P}$ 16.8 Hz, PCH_3), 1.5 - 2.2 (m, norbornyl).

Trinorborn-1-yl phosphite (1.23 g, 0.0034 mol) and methyl iodide (0.576 g, 0.004 mol) mixed in anhydrous ether (10 cm^3) were left standing at room temperature. The crystals which separated out over a period of 4 weeks were collected as three crops, washed several times with ether by decantation and dried in *vacuo* to afford the phosphonium iodide (75) (1.39 g, 81.3 %) as a white plates, m.p. 145-147 °C, (Found: C, 52.3; H, 7.4; $C_{22}H_{36}O_3PI$ requires: C, 52.2; H, 7.1 %), δ_P ($CDCl_3$) 36.9 (q, $^2J_{P-H}$ 16.4 Hz), δ_C($CDCl_3$) 97.3 (d, $^2J_{C-P}$ 11 Hz, norbornyl C-1), 42.8 (d, $^3J_{C-P}$ 3.7 Hz, norbornyl C-7), 34.2 (d, $^3J_{C-P}$ 3.0 Hz, norbornyl C-2,6),

33.0 (norbornyl C-4), 29.8 (norbornyl C-3,5), 16.1 (d, $^{1}J_{C-P}$ 130 Hz, PCH_3),, δ_H ($CDCl_3$) 2.51 (d, $^{2}J_{H-P}$ 16.2 Hz, PCH_3), 1.54 - 2.25 (m, norbornyl), ν_{max} 2985, 2880, 1320, 1085, 1060 cm^{-1}, m/z (FAB) 379 (P^{+} ion, 100 %), 285 (12.9 %), 253 (4.1 %), 95 (16.3 %).

2,2,2-Triphenylethoxy(diphenyl)methylphosphonium iodide (76):

Methyl iodide (0.0328 g, 0.00023 mol) was added to 2,2,2-triphenylethyl diphenylphosphinite (0.1059 g, 0.00023 mol) in deuterochloroform (0.5 cm^{3}) in a ^{1}H n.m.r. tube and the extent of the reaction was monitored at suitable intervals by comparing the decreasing signal for the methylene protons in 2,2,2-triphenylethyl diphenylphosphinite (δ_H 4.8, d, $^{3}J_{H-P}$ 5.4 Hz, CH_2OP) to the increasing signal for the methylene protons in the phosphonium iodide (δ_H 5.4, d, $^{3}J_{H-P}$ 4.2 Hz, CH_2OP) as it was formed. The following results were obtained:

Products	Approx. composition (mole %) at reaction time			
	7 min	2.1 h	23 h	44 h
$(C_6H_5)_3CCH_2OP(C_6H_5)_2$	58	35	14	-
$(C_6H_5)_3CCH_2O\overset{+}{P}(C_6H_5)_2CH_3\ I^-$	42	65	86	90
$(C_6H_5)_2P(O)CH_3$ (δ_H 2.26, d, $^2J_{H-P}$ 13.2 Hz, PCH_3)	-	-	-	10

After 44 h of mixing, the chloroform was evaporated at reduced pressure and the oily residue triturated with anhydrous ether to give a yellowish solid which was washed several times with anhydrous ether by decantation and dried in *vacuo* to afford the methylphosphonium iodide (76) (0.1 g, 72.2 %), m.p. 114-116 °C, δ_P ($CDCl_3$) 72.7, ν_{max} (KBr disc) 1590, 1490, 1435, 1320, 1130 - 1120, 1055, 1035, 1010, 990 cm^{-1}, δ_H ($CDCl_3$) 3.11 (d, $^2J_{H-P}$ 13.2 Hz, PCH_3), 5.38 (d, $^3J_{H-P}$ 4.2 Hz, CH_2OP).

3.8 Decomposition of quasiphosphonium salts:

Trinorborn-1-yloxy(phenacyl)phosphonium bromide (57):

The phosphonium bromide (0.0785 g, 0.00014 mol) in deuterochloroform (0.5 cm^3) sealed in an n.m.r. tube was heated in an oil bath at 132 °C for 20 h. The ^{31}P n.m.r. spectrum of the cooled mixture showed the presence of the phosphonium bromide (57) (δ_P 26.6, ca. 67 mole %), dinorborn-1-yl phenacylphosphonate (δ_P 13.4, ca. 31 mole %) and two unidentified compounds: (δ_P 17.5, ca. 1.0 mole %; δ_P 11.9, ca.1.0 mole %).

The phosphonium bromide (0.6402 g, 0.0011 mol) in deuterochloroform (3.0 cm^3) was divided equally into six sealed n.m.r. tubes and the tubes were placed in an oil bath thermostatted at 148.5 °C. A tube was removed at suitable intervals, cooled rapidly to room temperature and the extent of the decomposition was followed with ^1H n.m.r. by comparing the decreasing methylene protons in the phosphonium bromide (57) (δ_H 5.2, d, $^2J_{H-P}$ 19 Hz, PCH_2) to the increasing methylene protons in dinorborn-1-yl phenacylphosphonate [δ_H 3.6, d, $^2J_{H-P}$ 22.8 Hz, $P(O)CH_2$] as it was formed (for full characterisation see page 166). The following results were obtained:

Reaction time (h)	Approx. composition (mole %)	
	$(C_{20}H_{31}O)_3\overset{+}{P}CH_2COC_6H_5\ Br^-$	$(C_{20}H_{31}O)_2P(O)CH_2COC_6H_5$
1.21	76	24
1.83	74	26
2.25	69	31
3.48	59	41
6.05	39*	61

* Plus unidentified signal overlapping with that for the phosphonium salt at δ_H 5.2

The ^{31}P n.m.r. spectrum of the n.m.r. tube mixture after 6.1 h, of heating showed the presence of the phosphonium bromide (57) (δ_P 26.5, t, $^2J_{P-H}$ 18.2 Hz, *ca.* 33 mole %), dinorborn-1-yl phenacylphosphonate (δ_P 13.5, t, $^2J_{P-H}$ 23.2 Hz, *ca.* 40 %), trinorborn-1-yl phosphate (δ_P -10.5, *ca.* 1 mole %), and three unidentified compounds: (δ_P 18.2, d, J_{P-H} 8.9 Hz, *ca.* 16 mole %; δ_P 12.3, s, *ca.* 11 mole %; δ_P -14.2, *ca.* 1.0 mole %).

The tubes were further heated at 148.5 °C for 24 h, for complete decomposition, the contents poured into a flask and the chloroform evaporated at reduced pressure to give an oil which solidified on standing. The solid was dissolved in anhydrous acetone (2 cm^3) and the solution triturated with dropwise addition of anhydrous hexane. The dark oily product

which separated out first was discarded and the resulting clear yellowish solution was concentrated down at reduced pressure to give a solid which was washed with hexane (3 x 2 cm^3) by decantation and dried in *vacuo* to afford dinorborn-1-yl phenacylphosphonate (83) (0.183 g, 49.8 %), m.p. 101-103 °C, (Found: C, 67.3; H, 7.6; $C_{22}H_{29}O_4P$ requires C, 68.0; H, 7.5 %), δ_P ($CDCl_3$) 13.4 (t, $^2J_{P-H}$ 23.1 Hz), δ_H ($CDCl_3$) 1.34 - 2.1 (br.m, norbornyl), 3.57 [2H, d, $^2J_{P-H}$ 22.2 Hz, P(O)CH_2], 7.54 (m, 3H, Ar), 8.0 (m, 2H, Ar), δ_C ($CDCl_3$) 192.4 (d, $^2J_{C-P}$ 7.3 Hz, C=O), 137.1 (ArC-1), 133.3 (ArC-4), 129.3 (ArC-2,6), 128.5 (ArC-3,5), 89.9 (d, $^2J_{C-P}$ 7.9 Hz, norbornyl C-1), 42.2 (d, $^3J_{C-P}$ 4.3 Hz, norbornyl C-7), 41.5 [d, $^1J_{C-P}$ 130 Hz, P(O)CH_2], 34.0 (d, $^3J_{C-P}$ 2.4 Hz, (norbornyl C-2,6), 33.3 (norbornyl C-4), 29.7 (norbornyl C-3,5), ν_{max} (KBr disc) 2980, 2880, 1680, 1605, 1585, 1455, 1425, 1325, 1280, 1080, 1025, 1015, 945, 900 cm^{-1}, m/z 388 (M^+, 3.3 %), 351 (24 %), 277 (23.6 %), 105 (18.1 %), 103 (14.7 %), 95 (26.5 %), 85 (83.5 %), 83 (100 %), 77 (18.6 %), 70 (22.3 %), 67 (19.4 %). Evaporation of the solvent from the mother liquor gave an oily product which solidified on standing (0.23 g). ^{31}P.n.m.r. showed the presence of dinorborn-1-yl phenacylphosphonate (δ_P 13.5, *ca.* 94 mole %) and an unidentified compound (δ_P 9.9, *ca.* 6 mole %).

Trinorborn-1-yloxy-1-(p-nitrophenyl)vinyloxyphosphonium chloride (63):

The phosphonium chloride (0.426 g, 0.00075 mol) in deuterochloroform (3.0 cm^3) was divided equally into six sealed n.m.r. tubes and the tubes were placed in a thermostatted oil bath at 148.5 °C. The extent of disappearance of the vinyl protons in the phosphonium chloride (δ_H 5.4, dd, $=CH_A$, δ_H 6.3, dd, $=CH_B$) was followed by ^1H n.m.r. at suitable intervals as for the phosphonium bromide (57) in the above experiment. The ^1H n.m.r. spectrum after 1.4 h of heating showed no vinyl protons but the presence of signals at δ_H 3.3 (s, ≡CH and δ_H 2.6 (s, $COCH_3$ from p-nitroacephenone) was observed. Further heating showed no change in the spectrum. The ^{31}P and ^{13}C n.m.r. spectra of the mixture showed the presence of trinorborn-1-yl phosphate [δ_P -10.2, δ_C 29.7 (C-3,5), 33.4 (d, $^3J_{C-P}$ 4.0 Hz, C-2,6) 33.7 (C-4), 42.0 (d, $^3J_{C-P}$ 4.1 Hz, C-7), 89.1 (d, $^2J_{C-P}$ 7.5 Hz, C-1)] and p-nitrophenylacetylene [δ_C (9.0 mg $Cr(acac)_3$ added) 147.6 (ArC-4), 133.2 (ArC-2,6), 129.0 (ArC-1), 123.7 (ArC-3,5), 82.9 (≡CH), 81.7 (-C≡)], which agree well with reported values.[65] The ^{31}P n.m.r. spectrum also showed the presence of an unidentified compound (δ_P -13.4, *ca.* 4.0 mole %).

Trinorborn-1-yloxy(methyl)phosphonium iodide (75):

The phosphonium iodide (0.921 g, 0.0018 mol) and anhydrous benzene (0.1 cm^3) (internal standard) in deuterochloroform (3.4 cm^3) was divided equally into six sealed n.m.r. tubes and the tubes were placed in an oil bath thermostatted at 149 °C. The extent of the decomposition was followed by ^1H n.m.r. at suitable intervals as in the above experiment by comparing the decreasing methyl doublet in the phosphonium iodide (75) (δ_H 2.43, d, $^2J_{H-P}$ 16.2 Hz) to the benzene signal (δ_H 7.35). No significant change in the methyl doublet signal was observed after 8.2 h of heating. The ^{31}P n.m.r. spectrum after 24.6 h of heating showed the presence of the phosphonium iodide (75) (δ_P 36.5, *ca.* 71 mole %) and dinorborn-1-yl methylphosphonate (84) (δ_P 24.6, q, $^2J_{P-H}$ 17.6 Hz, *ca.* 29 mole %, for full characterisation see page 169).

The tubes were heated for a further 48 h, at 149 °C when ^1H n.m.r. of the mixture showed a large amount of the phosphonium iodide (85) still present. The tubes were again heated for a further 72 h at 150 °C and the contents poured into a flask and the solvent evaporated off. The residue was triturated with anhydrous ether to give a reddish brown solid which was washed with ether by decantation and dried in *vacuo* to afford the phosphonium iodide (0.38 g, 41 %), δ_P ($CDCl_3$) 35.5. The ether from the extract and washings was evaporated in *vacuo* to give a

reddish brown oil (0.13 g, 25 %). ^{31}P n.m.r. of the oil showed, the presence of dinorborn-1-yl methylphosphonate only, δ_P ($CDCl_3$) 24.4 (q, $^2J_{P-H}$ 17.6 Hz), ν_{max} 2970, 2880, 1460, 1330, 1275, 1180, 1090, 1030, 1000, 950, 760 cm^{-1}, δ_C ($CDCl_3$) 97.4 (d, $^2J_{C-P}$ 11.0 Hz, norbornyl C-1), 42.9 (d, $^3J_{C-P}$ 4.3 Hz, norbornyl C-7), 34.1 (d, $^3J_{C-P}$ 3.1 Hz, norbornyl C-2,6), 32.8 (norbornyl C-4), 29.8 (norbornyl C-3,5), 15.4 [d, $^1J_{C-P}$ 130 Hz, $P(O)CH_3$], δ_H ($CDCl_3$) 1.4 - 2.1 [br.m, norbornyl), 1.46 [d, $^2J_{P-H}$ 16.8Hz, $P(O)CH_3$], m/z 284 (M^+, 32.2 %), 256 (17.1 %), 255 (100 %), 191 (15.9 %), 161 (12.1 %), 97 (15.8 %), 95 (54 %).

3.9 Attempts to trap the betaine (67) from the reaction of trinorborn-1-yl phosphite and α-chloro-p-nitroacetophenone.

With methanesulphonyl chloride:

α-Chloro-p-nitroacetophenone (0.0307g, 0.0001 mol) and methanesulphonyl chloride (0.0169 g, 0.0001 mol) in deuterochloroform (0.3 cm^3) were added to trinorborn-1-yl phosphite (0.0539 g, 0.0001 mol) in deuterochloroform (0.2 cm^3) in an n.m.r. tube and the reaction monitored by ^1H n.m.r. The spectrum after 7 min of mixing showed the presence of unreacted α-chloro-p-nitroacephenone (δ_H 4.8, s, CH_2Cl), methanesulphonyl chloride (δ_H 3.66, s, CH_3) and signals at δ_H 3.0 and δ_H 0.84. No change was seen in the spectrum after a further 18 h. ^{31}P n.m.r. of the mixture showed the presence of a phosphorus-containing compound at δ_P 49.7, (*ca.* 22 mole %) and trinorborn-1-yl phosphate (δ_P -10.6, *ca.* 78%).

With trifluoroacetic acid:

α-Chloro-p-nitroacetophenone (0.04 g, 0.0002 mol) and trifluoroacetic acid (0.0244 g, 0.0002 mol) in deutero-chloroform (0.35 cm^3) were added to trinorborn-1-yl phosphite (0.0781 g, 0.0002 mol), in deuterochloroform (0.3

cm^3) in an n.m.r. tube and the reaction followed by ^1H n.m.r. The spectrum after 24 h gave multiplets at δ_H 5.4 and δ_H 6.0 due to the vinyl protons in trinorborn-1-yloxy-1-(p-nitrophenyl)vinyloxyphosphonium chloride (63). No other signal was observed during the course of the reaction. ^{31}P n.m.r. of the reaction mixture showed the presence of dinorborn-1-yl phosphite (δ_P -0.2, *ca.* 30 mole %), unidentified compounds (δ_P -12.7, *ca.* 6 mole %, δ_P -14.2, *ca.* 10 mole %) and the vinyloxyphosphonium chloride (63) (δ_P -17.0, *ca.* 54 mole %).

<u>With methanol:</u>

α-Chloro-p-nitroacetophenone (0.044 g, 0.0002 mol) was added to trinorborn-1-yl phosphite (0.0778 g, 0.0002 mol) in anhydrous methanol (0.5 cm^3, 10 % methanol in methanol-d_4) in an n.m.r. tube and the reaction followed by ^1H n.m.r. The spectrum after 2 h showed the presence of the vinyl protons, δ_H 5.7 and δ_H 5.6 (m, $=CH_AH_B$), and signals at δ_H 3.7 (s), and δ_H 2.0 (br, s). ^{31}P n.m.r. of the mixture showed the presence of dimethyl 1-(p-nitrophenyl)vinyl phosphate (δ_P -4.6, *ca.* 76 mole %) (see page 150, Table 12) and the vinyloxyphosphonium chloride (63) (δ_P -17.2, *ca.* 24 mole %).

With benzoyl chloride:

α-Chloro-p-nitroacetophenone (0.0455 g, 0.0002 mol) and benzoyl chloride (0.0304 g, 0.0002 mol) in deuterochloroform (0.5 cm^3) were added to trinorborn-1-yl phosphite (0.0789 g, 0.0002 mol) in an n.m.r. tube and the reaction followed by ^1H n.m.r. The spectrum after 3.2 h of mixing showed the presence of the vinyloxyphosphonium chloride (63) only. After 28.2 h of mixing, two small additional signals at δ_H 4.1 and δ_H 4.5 were observed. ^{31}P n.m.r. after 2 mth at room temperature showed the presence of the vinyloxy-phosphonium chloride (63) (δ_P -17.4, *ca.* 60 mole %), trinorborn-1-yl phosphate (δ_P -11.2, *ca.* 26 mole %) and unidentified compounds (δ_P 14.8, *ca.* 9 mole % and δ_P 30.8 mole %, *ca.* 5 mole %). ^1H n.m.r. after 2 mth showed in addition to the vinyl protons (δ_H 5.5 and δ_H 6.2) in vinyloxyphosphonium chloride unidentified signals at δ_H 4.3 and δ_H 3.9 together with a signal at δ_H 2.7 due to p-nitroacetophenone.

With hydrogen chloride:

Trinorborn-1-yl phosphite (0.405 g, 0.001 mol) in deuterochloroform (2.5 cm^3) was saturated with anhydrous hydrogen chloride (0.0705 g, 0.002 mol). ^{31}P n.m.r. of the mixture at 27 °C (n.m.r. spectrometer temperature) gave a

broad singlet at δ_P 14.8 due to the protonated trinorborn-1-yl phosphite [$(C_7H_{11}O)_3\overset{+}{P}H$ $\bar{Cl}$]. No change was observed in the chemical shift on decreasing the spectrometer temperature from 27° to -55 °C. The mixture was allowed to warm to room temperature and α-chloro-p-nitroacetophenone (0.2313 g, 0.001 mol) was added. The ^{31}P n.m.r. spectrum at 27 °C (spectrometer temperature) after one hour showed the presence of the protonated trinorborn-1-yl phosphite (δ_P 14.5, *ca.* 91 mole %), dinorborn-1-yl phosphite (δ_P -0.09, $^1J_{P-H}$ 698.9 Hz, *ca.* 7 mole %), and two unidentified compounds: (δ_P 0.9, *ca.* 1.0 mole % and δ_P -12.6, *ca.* 1.0 mole %). No change was seen in the spectrum after a further 20 h. ^{31}P n.m.r. of the mixture at -55 °C (spectrometer temperature) after two weeks at room temperature showed the presence of the vinyloxyphosphonium chloride (63) (δ_P -16.0, *ca.* 67 mole %), trinorborn-1-yl phosphate (δ_P -10.5, *ca.* 23 mole %) and two unidentified compounds: (δ_P 16.6, *ca.* 7 mole % and δ_P 32.1, *ca.* 3 mole %). ^1H n.m.r. of the mixture at ambient temperature gave signals at δ_H 1.4 - 2.2 (br, norbornyl), δ_H 4.9 (s, CH_2Cl in α-chloro-p-nitroacetophenone), 8.3 (br, Ar), 9.4 (br s, HCl, exchanged in D_2O). No vinyl protons were observed. ^{13}C n.m.r. at ambient temperature, showed the presence of α-chloro-p-nitroacetophenone [δ_C ($CDCl_3$) 46.6 (CH_2Cl), 124.1 (ArC-3,5), 130.0 (ArC-2,6), 138.9 (ArC-1), 150.7 (ArC-NO_2), 190.5 (C=O)], and probably protonated trinorborn-1-yl phosphite [δ_C ($CDCl_3$) 29.5 (norbornyl

C-3,5), 33.0 (norbornyl C-4), 33.8 (d, $^{3}J_{C-P}$ 3.0 Hz, norbornyl C-2,6), 42.2 (d, $^{3}J_{C-P}$ 4.3 Hz, norbornyl C-7), 97.48 (d, $^{2}J_{C-P}$ 9.1 Hz, norbornyl C-1). ^{31}P n.m.r. of the mixture rerun after two months at room temperature and run at ambient spectrometer temperature showed the presence of the vinyloxyphosphonium chloride (δ_P -17.4, *ca.* 59 mole %), tirnorborn-1-yl phosphate (δ_P -10.9, *ca.* 6 mole %) and dinorborn-1-yl phosphite (δ_P -0.54, *ca.* 35 mole %).

Attempts to recover trinorborn-1-yl phosphite from the phosphite hydrogen chloride mixture by pumping off the chloroform and hydrogen chloride in *vacuo* for 10 h resulted in a white gummy solid being obtained. ^{31}P n.m.r. ($CDCl_3$) at -55 °C n.m.r. (spectrometer temperature), of the solid showed the presence of the trinorborn-1-yl phosphite (δ_P 142.2, *ca.* 29 mole %), protonated trinorborn-1-yl phosphite (δ_P 19.7, d, $^{1}J_{P-H}$ 829.9 Hz, *ca.* 38 mole %), dinorborn-1-yl phosphite (δ_P 1.0, d, $^{1}J_{P-H}$ 687.1, *ca.* 25 mole %) and trinorborn-1-yl phosphate (δ_P -10.4, *ca.* 8 mole %).

Attempted solvolysis of trinorborn-1-yloxy-1-(p-nitrophenyl)vinyloxyphosphonium chloride (63) in methanol.

The vinyloxyphosphonium chloride (0.05 g, 0.00009 mol) was dissolved in anhydrous methanol (0.5 cm^3, 10 % methanol in methanol-d_4) in an n.m.r. tube and the sealed tube left

at room temperature. ^{31}P n.m.r. of the solution after two months showed no change in the vinyloxyphosphonium chloride signal (δ_P -17.5).

Reaction of methanesulphonyl chloride with trinorborn-1-yl phosphite.

Methanesulphonyl chloride (0.0266 g, 0.00023 mol) was added to trinorborn-1-yl phosphite (0.0846 g, 0.00023 mol) in deuterochloroform in an n.m.r. tube and the reaction followed by ^1H n.m.r. The spectrum after 17 min of mixing showed the presence of unreacted methanesulphonyl chloride (δ_H 3.7, s, CH_3SO_2) and unidentified signals at δ_H 3.4 (s) and δ_H 3.0 (s). No change was seen in the spectrum after a further 23 h. ^{31}P n.m.r. of the mixture showed the presence of an unidentified compound: (δ_P 49.7, *ca.* 24 mole %), and trinorborn-1-yl phosphate (δ_P -10.4, *ca.* 76 mole %).

3.10 Reaction of trimethyl phosphite with α-iodoacetone in the presence of silver perchlorate.

General method of monitoring the reaction of α-iodoacetone with trimethyl phosphite and silver perchlorate:

Anhydrous silver perchlorate (see Table 15) was added to freshly distilled trimethyl phosphite (see Table 15) in anhydrous benzene (2 cm^3, 85 % in benzene-d_6) in an n.m.r. tube and the reaction monitored by ^{31}P n.m.r. over a period of time. The mixture was then added to iodoacetone (see Table 15) in benzene (0.5 cm^3) in an n.m.r. tube under anhydrous condition and the monitoring continued over a peroid of time. The silver iodide formed was removed by decantation and quinoline (see Table 15) was added to the solution. Monitoring of the reaction was contiuned. Results of the experiments are summarised in Table 15. The ^{31}P n.m.r. results of the effect of silver perchlorate on the expected products and side products from the reaction of trimethyl phosphite with iodoacetone alone are summarized in Table 16.

Table 15

^{31}P n.m.r. results of the reaction of iodoacetone with trimethyl phosphite and silver perchlorate.

Reactants No	$(CH_3O)_3P$ [a] + $AgClO_4$		On adding ICH_2COCH_3 [b]		On adding C_9H_7N [c]	
	Reaction time (min)	δ_P (Approx. mole %)	Reaction time (min)	δ_P (Approx. mole %)	Reaction time (min)	δ_P (Approx. mole %)
1	5	127.1, 14.8 (63) (37)	65	2.2, -10.3 (51) (49)	30	2.2, -10.4 (62) (38)
			96 h	1.8, -10.7 (62) (38)		
2	25	127.3, 36.3 (95) (5)	7	128.1, 36.3, 2.2, (95) -10.2, -10.9, -20.7		
			20	128.1, 36.3, 33.8, (38) (23) (18) 1.7, -10.8 (10) (12)		
			40	128.1, 36.5 (29) (18) 1.8, -10.4 (18) (35)		
			70	128.6, 1.8, -10.2 (31) (23) (46)		
			24 h	128.4, 1.8, -10.4 (19) (13) (68)		

Table 15 continued

Reactants No	$(CH_3O)_3P$ [a] + $AgClO_4$		On adding ICH_2COCH_3 [b]		On adding C_9H_7N [c]	
	Reaction time (min)	δ_P (Approx. mole %)	Reaction time (min)	δ_P (Approx. mole %)	Reaction time (min)	δ_P (Approx. mole %)
3	25	127.5, 36.3 (95) (5)	3	127.5, 36.5, 34.0	5	129.6, 1.9, -10.9
					40	130.1, -11.1
			10	128.3, 36.5, -10.5 (57) (10) (30)	24 h	131.1, 2.2, -10.4 (90) (4) (7)
			15	128.2, 36.5, -10.5 (48) (21) (30)	2 wk	9.0, 2.3, 1.5, (17) (35) (10) -10.3 (38)
			22	128.3, -10.5 (60) (40)		
			30	128.2, -10.5 (57) (43)		
4	25	127.4, 16.2 (92) (8)	30	1.8, -10.5 [a] (26) (74)		

Table 15 continued

No	Reactants (g, mol)			
	$(CH_3O)_3P$	$AgClO_4$	ICH_2COCH_3	C_9H_7N
1	0.28, 0.0023	0.47, 0.0023[d]	0.37, 0.002	0.3, 0.0023
2	0.321, 0.0026	0.537, 0.0026[e]	0.476, 0.0026	
3	0.327, 0.0026	0.547, 0.0026[e]	0.486, 0.0026	0.341, 0.0026
4	0.315, 0.0025	0.527, 0.0025[f]	0.468, 0.0025	

[a] ^{31}P n.m.r. of $(CH_3O)_3P$ recorded before adding $AgClO_4$, δ_P 140.3.

[b] AgI precipitated out immediately on adding ICH_2COCH_3.

[c] Reddish brown precipitate assumed to be $C_9H_7NCH_3$ ClO_4 was obtained.

[d] $AgClO_4$ dried in silica gel dessicator under *vacuo* for 18 h.

[e] $AgClO_4$ dried as in (b) for 40 h, and mixing of reactants carried out under dried nitrogen.

[f] $AgClO_4$ dried by Radell *et. al.* procedure.[66]

[g] δ_H (solution) 3.48 (d, J_{H-P} 12 Hz), 3.41 (d, J_{H-P} 11.4 Hz), 3.36 (d, J_{H-P} 11.4 Hz), 3.22 (s), 3.09 (ICH_2COCH_3), 1.74 (CH_3COCH_2I), 1.6 (s, pronounced signal), ν_{max} (solution) 2990, 1715, 1450, 1360, 1290, 1220, 1060 - 1040, 850, 735 cm^{-1}.

Table 16

The effect of $AgClO_4$ on the ^{31}P n.m.r. of the expected products and side products from the reaction of trimethyl phosphite with iodoacetone in benzene-d_6:

Product	δ_P	δ_P with $AgClO_4$ [a]
$(CH_3O)_3P$	140.3	127.
$(CH_3O)_3P$	140.3	134.9 [b]
$(CH_3O)_2P(O)CH_3$	30.9	35.1 [c]
$(CH_3O)_2P(O)CH_2COCH_3$	21.8	25.5 (two layers obtained on mixing) [c]
$(CH_3O)_2P(O)H$	8.9	12.5
$(CH_3O)_3P(O)$	2.4	1.9 (pink ppt formed) [c]
$(CH_3O)_2P(O).O.C(CH_3)=CH_2$	-4.8	-5.1 (solution turned dark brown on standing) [c]

[a] 1 mol. equiv. of $AgClO_4$ used.

[b] 4 mol. equiv. of $AgClO_4$ used.

[c] No change was seen in the spectrum after a further 24 h.

Reaction of methyl iodide with silver perchlorate in benzene-d_6

Methyl iodide (0.051 g, 0.00036 mol) was added to anhydrous silver perchlorate (0.0744 g, 0.00036 mol) in benzene-d_6 (0.5 cm^3) in an n.m.r. tube and the reaction monitored by ^1H n.m.r. Formation of yellow precipitate was observed on mixing the reactants. The ^1H n.m.r. spectrum showed a complete conversion to methyl perchlorate (δ_H 3.14) [lit.[44] δ_H (CCl_4) 4.22], after 21 h of reaction time, with no other product detected.

Reaction of iodoacetone with silver perchlorate

Iodoacetone (0.076 g, 0.0004 mol) was added to a solution of anhydrous silver perchlorate (0.086 g, 0.0004 mol) in anhydrous benzene-d_6 (0.5 cm^3) in an n.m.r. tube and the reaction monitored by ^1H n.m.r. Two layers were obtained on mixing, with a dark brown precipitate gradually forming in the bottom layer. ^1H n.m.r. of the mixture after 6 min of mixing showed the presence of unreacted iodoacetone (δ_H 1.76, 3H, CH_3, δ_H 3.22, 2H, CH_2I), singlets at δ_H 2.86 and 4.86 with integration ratio 3:2 respectively (ca. 86 mole % with respect to unreacted iodoacetone) and at δ_H 7.9. An increase in the benzene signal (present in the benzene-d_6 used) at δ_H 7.2 was also observed. The ^1H n.m.r. spectrum

after 1.5 h showed no change in the reaction mixture, but the bottom layer was found to have solidified after 20 h of mixing with the ^1H spectrum showing the presence of only the unreacted iodoacetone.

Reaction of trimethyl phosphite with iodoacetone and silver perchlorate.

Iodoacetone (0.0906 g, 0.0005 mol) was added to a solution of anhydrous silver perchlorate (benzene-d_6 (0.5 cm^3) in an n.m.r. tube. The ^1H n.m.r. spectrum of the reaction was the same as that observed in the above experiment. Trimethyl phosphite (0.061 g, 0.005 mol) was added to the mixture after 20 min and the reaction monitored by ^1H n.m.r. Formation of yellow precipitate was observed on adding trimethyl phosphite. ^1H n.m.r. after 20 min showed the presence of singlets at δ 1.75, and δ 1.96 and overlapped signals at δ 3.3 - 3.8. The singlet at δ 1.96 disappeared after 24 h.

Preparation of dimethyl methylphosphonate:

Trimethyl phosphite (10.5 g, 0.085 mol) was added to methyl iodide (12.0 g, 0.085 mol) and the mixture heated under reflux for 5 h. Distillation of the mixture at 68 -

69 °C / 20 mm (lit.[67] b.p. 181 °C) afforded the dimethyl methylphosphonate (8.72 g, 83 %), δ_P (C_6D_6) 30.93, δ_H ($CDCl_3$) 1.45 [d, 3H, $^2J_{H-P}$ 18 Hz, P(O)CH_3], 3.72 (d, 6H, $^3J_{H-P}$ 11 Hz, CH_3O).

Preparation of trimethyl phosphate:

Anhydrous methanol (23.7 g, 0.74 mol) and dried pyridine (55.0 g, 0.69 mol) in anhydrous ether (150 cm^3) were added to a stirred solution of phosphorus oxychloride (35.7 g, 0.23 mol) in anhydrous ether (200 cm^3) cooled in ice, and the mixture stirred at room temperature for 18 h. The precipitate formed was filtered off, washed with ether and the solvent from the combined filtrate and washings evaporated at reduced pressure. Distillation of the residue at 42 °C / 1 mm (lit.[67] 197 °C) afforded the trimethyl phosphate (7.54 g, 23.3 %), δ_P ($CDCl_3$) 2.39, δ_H ($CDCl_3$ 3.77 (d, $^3J_{H-P}$ 10.8 Hz).

Preparation of dimethyl chlorophosphate:

Anhydrous methanol (14.9 g, 0.46 mol) and dried pyridine (36.8 g, 0.46 mol) in anhydrous ether (100 cm^3) were added to a stirred solution of phosphorus oxychloride (36.7 g,

0.24 mol) in anhydrous ether (100 cm^3) cooled in ice. Continuation of the procedure as in the above experiment afforded the chlorophosphate (2.3 g, 6.9 %) on distillation at 87 °C / 18 mm (lit.[69] 70 °C / 10 mm).

Preparation of tetramethyl pyrophosphate (96):[69]

Dimethyl chlorophosphate (2.3 g, 0.016 mol) and trimethyl phosphate (7.5 g, 0.053 mol) were heated at 130 °C for 2 h. Distillation of the mixture at 114 - 116 °C / 0.5 mm (lit[69] 106 - 108 °C / 0.3 mm) afforded the pyrophosphate (2.99 g, 80.4 %), δ_P ($CDCl_3$) -10.35 (the proton coupled spectrum showed a splitting pattern consistent with that reported in literature)[70].

Preparation of dimethyl 1-methylvinyl phosphate (98):[71]

Chloroacetone (5.81 g, 0.063 mol) was added dropwise to stirred trimethyl phosphite (7.79 g, 0.063 mol) at 65 °C and the mixture maintained between 60 - 70 °C for 5 h. Distillation at 84 - 86 °C / 11 mm (lit.[71] 84 - 85 °C / 9 mm) afforded the phosphate (6.26 g, 60 %) as a clear oil, δ_P ($CDCl_3$) -4.6, δ_H ($CDCl_3$) 1.94 (s, 3H, $CH_3C=$), 3.79 (d, 6H, $^3J_{H-P}$ 12 Hz, CH_3OP), 4.67 (dm, 2H, $=CH_2$).

Preparation of dimethyl acetonylphosphonate (99):[71]

Trimethyl phosphite (5.86 g, 0.047 mol) was added to a stirred solution of iodoacetone (8.64 g, 0.047 mol) in anhydrous benzene (10 cm^3) and the mixture maintained at 65 - 70 °C for 5 h. The mixture was cooled to room temperature and the methyl iodide and benzene evaporated in *vacuo*. The residue was distilled at 123.5 °C / 11 mm (lit.[71] 123 - 124 °C / 10 mm) to give the phosphonate (5.33 g, 68 %), δ_P ($CDCl_3$) 22.0, δ_H ($CDCl_3$) 2.3 (s, 3H, $COCH_3$), 3.14 (d, 2H, $^2J_{H-P}$ 24 Hz, $P(O)CH_2$), 3.78 (d, 6H, $^3J_{H-P}$ 12 Hz, CH_3OP).

3.11 X-ray structure analysis of trinorborn-1-yloxy (phenacyl)phosphonium bromide (57) and trinorborn-1-yloxy-1-(p-nitrophenyl)vinyloxyphosphonium chloride (63).

Trinorborn-1-yloxy(phenacyl)phosphonium bromide (57):

Crystals of the phosphonium bromide (57) were obtained directly *in situ* from the reaction of α-bromoacetophenone and trinorborn-1-yl phosphite in anhydrous ether (see section 3.7), in the form of white needles. Crystal size 0.56 × 0.51 × 0.16 mm; μ(Mo-K) = 15.12 cm^{-1} was used in data collection and the data were collected on a Phillips PW1100 four circle diffractometer with Mo-Kα radiation.

Crystal data: $C_{28}H_{30}BrO_4P$; M = 563; Monoclinic; a = 14.413(4), b = 9.996(3), c = 19.215(5) Å; β = 90.73(3) °; V = 2768.13 $Å^3$ (by least square refinement on diffractometer angles for 25 automatically centred reflections, λ = 0.71069 Å); space group P21/c; Z = 4; Dx = 1.35 g cm^{-3}.

Refinements with 1484 reflections [(I / σ(I) > 3.0)] converged to give R = 0.0985 and Rw = 0.0952.

Trinorborn-1-yloxy-1-(p-nitrophenyl)vinyloxyphosphonium chloride (63):

Crystals of the phosphonium chloride (63) were obtained directly *in situ* from the reaction of α-chloroacetophenone and trinorborn-1-yl phosphite in anhydrous ether (see section 3.7), in the form a yellowish brown fern like crystals. Crystal size 0.4 × 0.19 × 0.08 mm; μ(Mo-K) = 1.64 cm^{-1} was used in data collection as for above structure.

Crystal data: $C_{26}H_{26}ClNO_5P$; M = 563.5; Monoclinic; a = 9.288(3), b = 30.074(6), c = 11.894(3) Å; β = 98.69(3)°; V = 3284.12 $Å^3$ (by least square refinement on diffractometer angles for 25 automatically centerd reflections, λ = 0.71069 Å); space group P21/c; Z = 4; Dx = 1.139 g cm^{-3}.

Refinements with 4028 reflections [(I / σ(I) > 3.0)] converged to give R = 0.2087 and Rw = 0.21.

Chapter 4

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