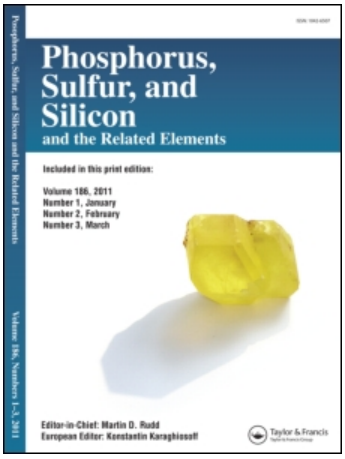

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ORGANOPHOSPHORUS CHEMISTRY TODAY

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England

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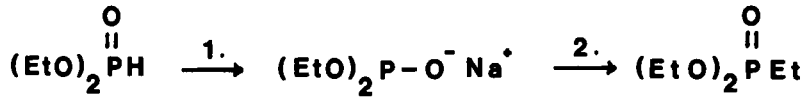
LANDMARKS IN ORGANOPHOSPHORUS CHEMISTRY

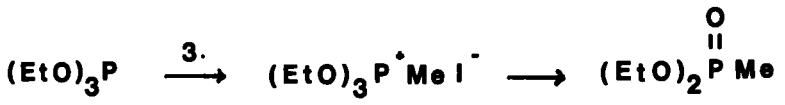
It is always instructive to recall the great names of chemistry and their contributions. This is particularly so in organophosphorus chemistry for within a dozen names one can review a century of endeavour in this field.

It is to A. Michaelis that we look for the foundation of the science of organophosphorus chemistry and his remarkable contributions in the late 1860's to the early 1900's to most aspects of preparative organic phosphorus chemistry are well known. The tervalent phosphorus compounds are key precursors to the majority of the classes of organophosphorus compounds and are important reagents in organic synthesis. This importance hinges on the nucleophilicity of phosphorus and this aspect was well explored by Michaelis. Two important reactions discovered by Michaelis may be highlighted. These involve the synthesis of dialkyl alkylphosphonates through nucleophilic displacement with dialkyl phosphite anion (Michaelis-Becker Reaction[1]) or trialkyl phosphites (Michaelis-Arbusov Reaction[2]). The preparation of these valuable synthetic reagents has recently become important because of their use in olefin-forming reactions.

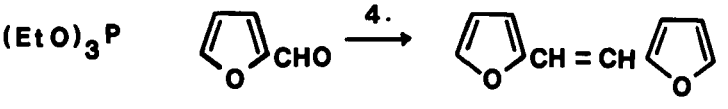
The name of A.E. Arbusov will be remembered for his detailed investigation[3] of the rearrangement that bears his name. However, his enormous contribution to the elaboration of synthetic methods and the unification of the basic principles of the reactions of organophosphorus chemistry cannot be too highly stressed. His foundation and development of the Russian School to rival the German School of Michaelis is his tribute. The tradition of Arbusov has been continued by the meticulous work of B.A. Arbusov and M.I. Kabachnik. B.A. Arbusov has been particularly interested in nucleophilic reactions of trivalent organophosphorus compounds and the isolation of unusual products from complex reaction mixtures. His observation of the production of difuryl ethylene when furfural is heated with triethyl phosphite remains[4] one of the few examples of complete removal of oxygen from a carbonyl



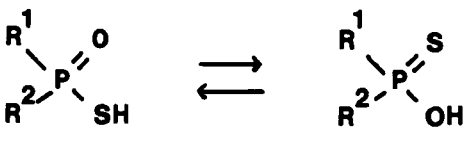
Michaelis - Becker 1897



Michaelis 1898
Arbusov 1906

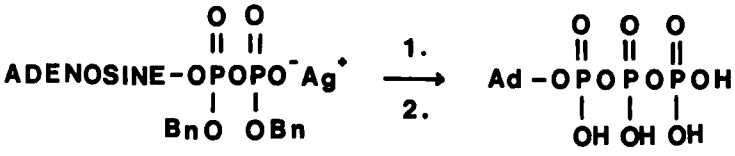


Arbusov 1960



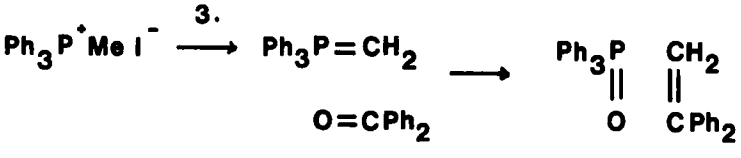
Kabachnik 1960

1. Na 2. EtI 3. MeI

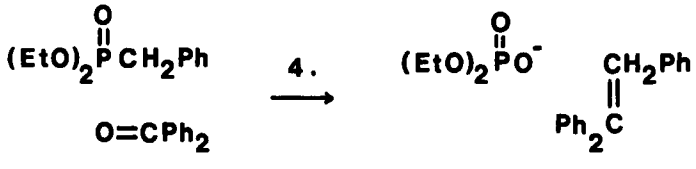


Todd 1949

Mann 1952



Wittig 1953



Horner 1958

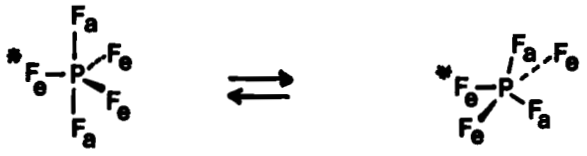
1. $(BnO)_2P(O)Cl$ 2. H_2 3. PhLi 4. $NaNH_2$

group by trivalent phosphorus. Phosphite deoxygenation has since become an important reaction in synthetic organic chemistry[5]. Kabachnik has been instrumental in developing the physical organic chemistry of phosphorus. Typical of his work has been correlation[6] of pKa values of phosphines with substituent constants determined from the pKa of phosphonic acids and the estimation[7] of the position of tautomeric equilibrium in the thionic acids by the use of an empirical free energy relationship of the Hammett type.

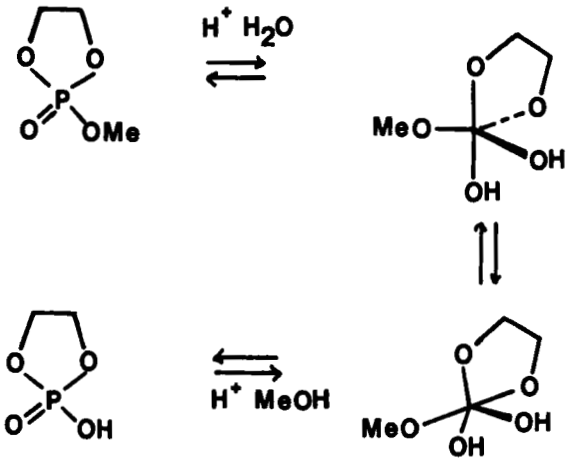
At this time, the English School of Organophosphorus Chemistry was developing under A.R. Todd and F.G. Mann. Todd was interested in the synthesis of organophosphorus compounds of biochemical origin and developed new methods of phosphorylation for the synthesis of components of nucleic acids. One landmark was the first chemical synthesis of ATP[8]. Mann carefully prepared a wide range of phosphines and studied their displacement and addition reactions. An example from this work is one of the first additions[9] of a phosphine to an activated double bond.

The most important discovery to emerge from the recent history of preparative organophosphorus chemistry is the observation[10] by G. Wittig that phosphorus ylides react with ketones to give olefins. This is undoubtedly one of the most valuable chemical reactions ever reported and in its five individual steps, illustrates why organophosphorus compounds possess such a diverse and synthetically useful chemistry. L. Horner more recently reported[11] that a similar olefination could be achieved using phosphonate stabilised carbanions and this variation has proved a useful supplement to the Wittig reaction with the advantages of increased carbanion reactivity and greater selectivity for E-alkene formation.

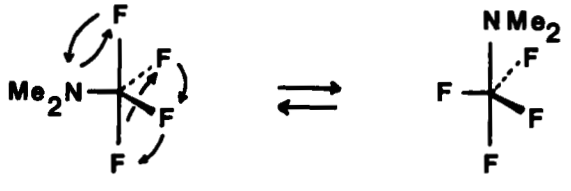
Modern mechanistic organophosphorus chemistry has been shaped by the synthesis and stereochemical analysis of pentavalent phosphorus compounds containing five ligands attached to the central phosphorus atom and the acknowledged role of these species as intermediates in many reactions. Thus Berry suggested[12] that



Berry 1960



Westheimer 1966



Ugi , Ramirez 1970

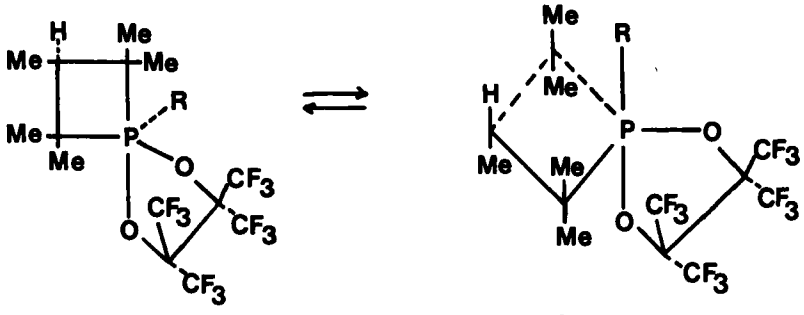
the fluorine atoms of trigonal bipyramidal PF_5 are rapidly equilibrating by Pseudorotation in order to explain that only one kind of fluorine is observable in the NMR spectrum.

Westheimer applied[13] the concept of pseudorotation to trigonal bipyramidal intermediates in the hydrolysis of methyl ethylene phosphate and was able to explain how ring strain could accelerate the rate of reaction (an order of 10^6 times over that of trimethyl phosphate) especially since 30% hydrolysis occurs without ring-opening. This rationalisation of the mechanism of phosphate ester hydrolyses has enabled a whole body of data in organophosphorus reactions to be explained and has established the preeminence of the Harvard group in this field.

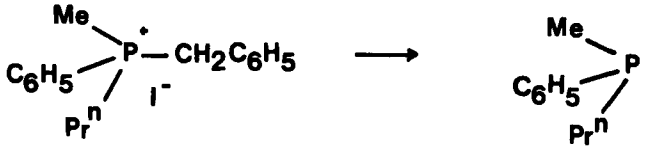
An alternative intramolecular exchange process may be used to fit the experimental data on pentacoordinated organophosphorus compounds and this is the Turnstile Rotation process[14] favoured by Ugi and Ramirez.

Although in an attempt to distinguish between Berry pseudorotation and turnstile rotation the groups of Ugi and Ramirez were able to confirm the latter process for certain polycyclic caged oxyphosphoranes, their major contribution must be the careful synthesis and exploration of the reactions of a wide variety of novel pentacovalent phosphoranes. Mention here must also be made of the valuable work of Trippett who has been responsible for the synthesis of many novel compounds and the development of new reactions in this area of phosphorane chemistry. For example, variable-temperature ^{19}F NMR spectroscopy of phosphoranes derived from reaction of 1 substituted phosphetans with hexafluoroacetone has enabled[15] data to be accumulated on relative apicophilicities of different groups, invaluable in discussing organophosphorus reaction mechanisms.

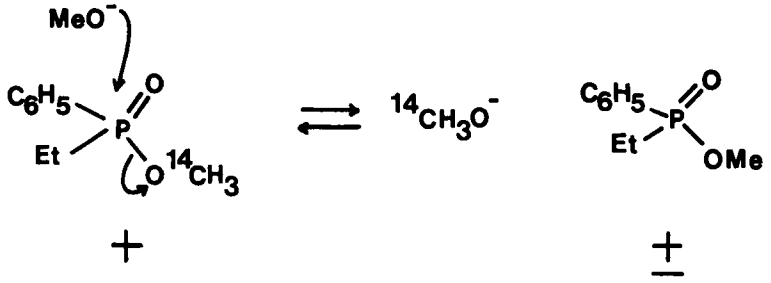
Finally, the preparation of organophosphorus compounds in optically active form has proved significant in the elucidation of a number of reaction mechanisms. We are indebted to Horner and colleagues for the synthesis[16] of optically active noncyclic



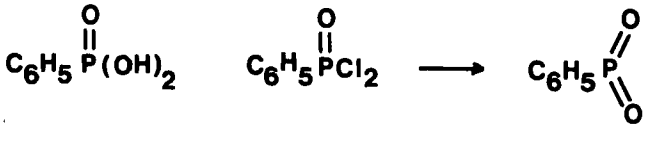
Trippett 1972



Horner 1961



Hudson 1962



Michaelis 1892

phosphines. Their elegant method involved the stereospecific electrolytic reduction of optically active phosphonium salts which proceeds by retention of configuration. Hudson was able to demonstrate[17] conclusively for the first time stereospecific reaction at the phosphoryl centre using optically active and ^{14}C-labelled methyl ethylphenylphosphinate. Thus the rate of racemisation was almost exactly twice the rate of loss of ^{14}C from the phosphinate showing that each act of chemical reaction proceeds with inversion of configuration.

These names span a century of research into organophosphorus chemistry and their contributions provide a useful framework within which I would like to fix my own personal view of the advances made in our field within the last three years. The rapidity of our recent progress may be illustrated by quoting some sentences from an important textbook of organophosphorus chemistry of the late 1950's.

"Perhaps the greatest fallacy resulting from use of the classicial valence-bond theory of organic chemistry in phosphorus chemistry is the over-simplification of structures by use of multiple bonds. Examples of such false structures which have been shown in the literature are Ph-P=P-Ph N≡P=NH N≡PCl_2 $O \geqslant P-ONa$."

It is unlikely that the above admonishment would have hindered the creativity of Michaelis who proposed[18] phenyldioxophosphorane for the structure of the product isolated from the reaction of benzenephosphonic acid with benzenephosphonic dichloride. These structural types, however, frequently appear in the literature of organophosphorus chemistry of the 1980's and are part of the renaissance that our subject is currently enjoying. In fact, what would have been regarded as the chemistry of the impossible in 1958 is the major theme of this presentation "Organophosphorus Chemistry Today".

Pπ-BONDED P^{III} AND P^{V} COMPOUNDS IN LOWER COORDINATION STATES

Early History

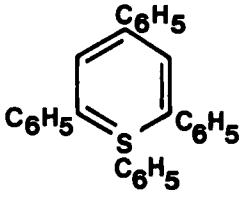
The ability of elements in the third period of the Periodic Table to enter into Pπ-Pπ bond formation is well known to be considerably reduced compared to, for example, carbon and nitrogen. This can be related to the poorer orbital overlap with the larger atoms such as phosphorus. In line with this thinking, as recently as 20 years ago, two-coordinate P^{III} compounds existed only in the realms of physics and the majority of organic chemists were unaware that a rich and exciting area of organophosphorus chemistry was soon to be discovered.

In 1961 Gier had reported[19] the synthesis of phosphaacetylene (1) when phosphine was passed through a low intensity graphite arc. Phosphaacetylene polymerises above - 130°C but was sufficiently stable to be characterised below that temperature. The C≡P infrared stretching frequency was assigned to 1265 cm^{-1}. Interestingly, the publication following Gier's was reporting[20] the synthesis of the novel thiabenzene (2). These authors commented that they were attempting to replace sulphur by phosphorus. Obviously they experienced some synthetic difficulties here, and it was not until 1966 when Märkl prepared[21] 2,4,6-triphenylphosphabenzene (3), that the first λ^3-phosphorin appeared. Mention must also be made here of Dimroth's synthesis of phosphamethincyanines, the first stable compounds containing delocalised C=P double bonds two years earlier[22]. Use was being made now of the stabilising influence of phenyl groups. Mention should also be made of the work of Burg and Mahler who prepared[23] (4) at low temperature by reacting $(PCF_3)_4$ with trimethylphosphine. (4), although unstable at room temperature, was characterised by an early use of ^{19}F and ^{31}P NMR spectroscopy. This early era of work may be closed by mention of Ashe's synthesis[24] of unsubstituted λ^3-phosphorin (5) by reaction of 1,4-dihydro-1,1-dibutylstannabenzene with phosphorus tribromide followed by base treatment to liberate free (5) from its salt.

$HC{\equiv}P$

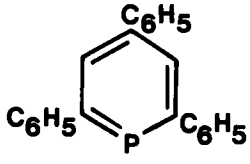
Gier 1961

(1)



Suld 1961

(2)



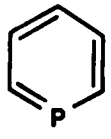
Märkl 1966

(3)

$Me_3P{=}PCF_3$

Burg 1961

(4)



Ashe 1971

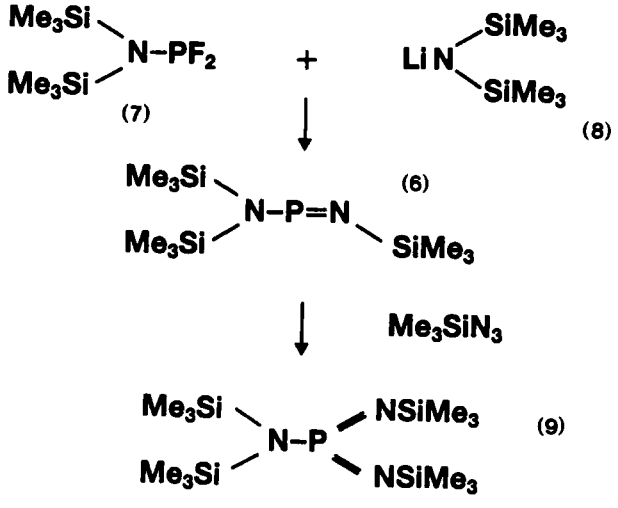
(5)

Spectral studies of (5), a stable liquid at room temperature, demonstrated its aromatic character.

Key Developments

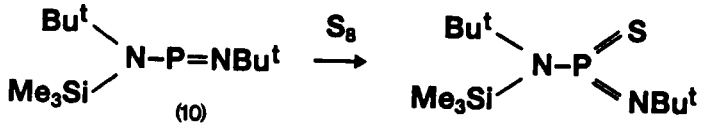
The infant field of organophosphorus compounds containing multiply-bound phosphorus of low coordination number was waiting for a new development which would enable these compounds to be isolated and studied at room temperature and this was provided by Niecke and Scherer who were the first to employ bulky substituents to stabilise such products. Thus Niecke and Flick in 1973 reported[25] the synthesis of the first phosphazene of coordination number 2 (6), a highly-reactive compound, stable below 0°C, by reaction of (7) with (8). Niecke[26] and Scherer[27] then proceeded to use this technique to prepare the first stable P^V compound with coordination number 3. (9), a distillable solid mp 36°C, was obtained by reaction of (6) with trimethylsilyl azide. Full spectroscopic characterisation of (9) was performed and reactions at the electrophilic phosphorus atom were described. Infra-red spectroscopy indicated the highly polar nature of the P=N bond. Scherer then extended[28] this development by the introduction of N-tert-butyl protection which proved to provide even greater stabilisation than N-trimethylsilyl groups. Trimethylsilyl(tert-butyl)amino(tert-butyl)iminophosphane (10) was formed in 30% yield by reaction of phosphorus tribromide with lithium (tert-butyl)(trimethylsilyl)amide. (10) unlike (6) only reacts with carbon tetrachloride at elevated temperature showing the improved stability of the P=N bond. Interestingly, reaction of (10) with sulphur at 80°C, gave iminothiophosphorane (11), the first isolable monomeric metathiophosphoric acid derivative in 80% yield. (11) is stable to at least 100°C.

At the same time, valuable work on the production of small unstable phosphaalkenes and phosphaacetylenes by pyrolysis continued. Kroto in 1976 produced[29] (12) by pyrolysis of dichloromethylphosphine at 1000°C and in 1978 (13) was prepared[30] by passing trifluoromethylphosphine vapour over solid potassium



Niecke, Flick 1973

Niecke, Flick 1974
Scherer, Kuhn 1974



Scherer, Kuhn 1974

$CH_2 = PCl$

Kroto 1976
(12)

$FC \equiv P$

Kroto 1978
(13)

hydroxide at room temperature. Photoelectron and microwave spectroscopy were used to establish product identity.

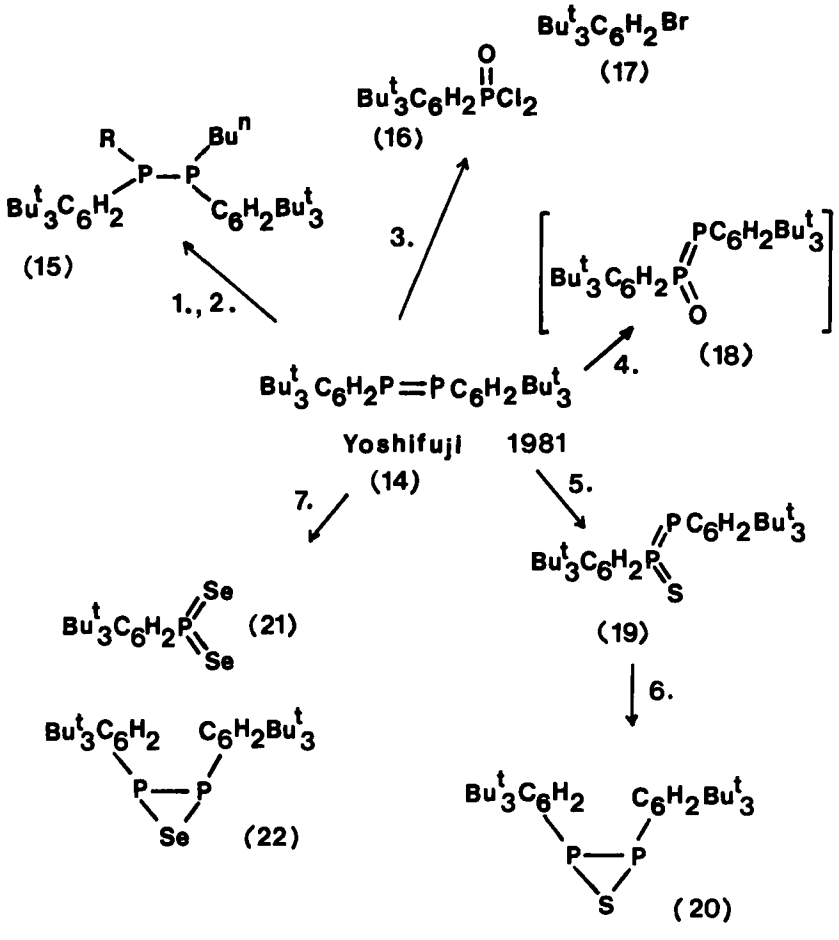
The techniques of bulky group stabilisation and elimination of trimethylsilyl halide thus led to the rapid growth of this area of chemistry and, if anything, growth since the meeting at Nice in 1983 has increased with the exploration of the chemistry of these fascinating compounds and the synthesis of ever more intriguing examples.

P=P Compounds

In 1981, Yoshifuji and Inamoto reported[31] the synthesis and structure of bis(2,4,6-tri-tert-butylphenyl)diphosphene (14), the first member of the novel class of compounds containing a P=P double bond, stabilised by the very bulky tri-tert-butylphenyl groups. The magnesium chloride elimination from the phosphonous dichloride coupled with the new highly stabilising "Yosh" group gave a new impetus to the developing field. The chemistry of the P=P has been rapidly developed.

- Reaction with n-butyllithium to give a phosphinophosphide followed by quenching with an alkyl halide to yield (15)[32].
- Reaction with halogen, presumably via addition to the P=P, to yield, in carbon tetrachloride (16) or (17)[33].
- Oxidation gave 2,4,6-tri-tert-butylphenylphosphine which is produced from the intermediate diphosphene oxide (18), a stable though rapidly hydrolysed, solid[34].
- Reaction with sulphur gave the first diphosphene sulphide (19) as a stable, crystalline solid[35]. Interestingly, (19) could be thermally or photochemically isomerised to the thiadiphosphirane (20).
- With elemental selenium, (14) is converted into a mixture of (21) and (22), both thermally stable[36].

After Yoshifuji's initial synthesis of diphosphene (14) momentum rapidly increased in the P=P field and other groups began to make important contributions. Escudié used[37] the



1. Bu^{n}Li 2. RBr 3. Cl_2 or Br_2

4. m-Cl $C_6H_4CO_3H$ 5. S_8 , Et_3N

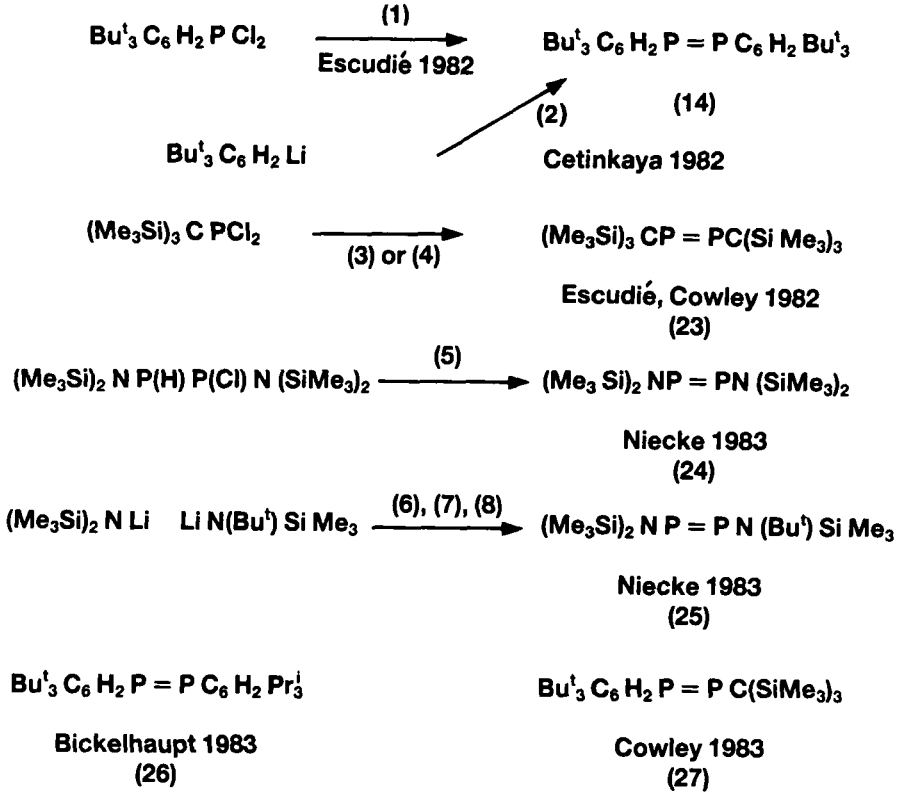
6. hν or heat 7 Se_n , Et_3N

trimethylsilyl halide elimination route to Yoshifuji's diphosphene (14) and Cetinkaya eliminated[38] lithium chloride. The new diphosphene (23) was prepared by Escudié[39] using lithium chloride elimination and by Cowley[40] using sodium chloride elimination. The larger tris(trimethylsilyl)methyl protecting groups in (23) proved responsible for differences[41] in reactivity between (14) and (23) towards electrophiles. At this time, Niecke was exploring the synthesis and properties of diaminodiphosphenes. (24)[42] and one of the first unsymmetrical diphosphenes (25)[43] were prepared by lithium chloride or triethylamine hydrochloride elimination. Unsymmetrical diphosphenes such as (26) were prepared[44] by Bickelhaupt, 1983 using magnesium cross-coupling of aryldihalophosphine and Cowley synthesised[45] (27) via his sodium naphthalenide approach. A more satisfactory method for preparing unsymmetrical diphosphenes was then developed by Cowley, 1983[46] and Yoshifuji, 1983[47] who reacted monoarylphosphines with alkyl or arylphosphonous dichlorides in the presence of DBU. Yields were high. (28) and (29) were obtained in 78% and 76% yields respectively.

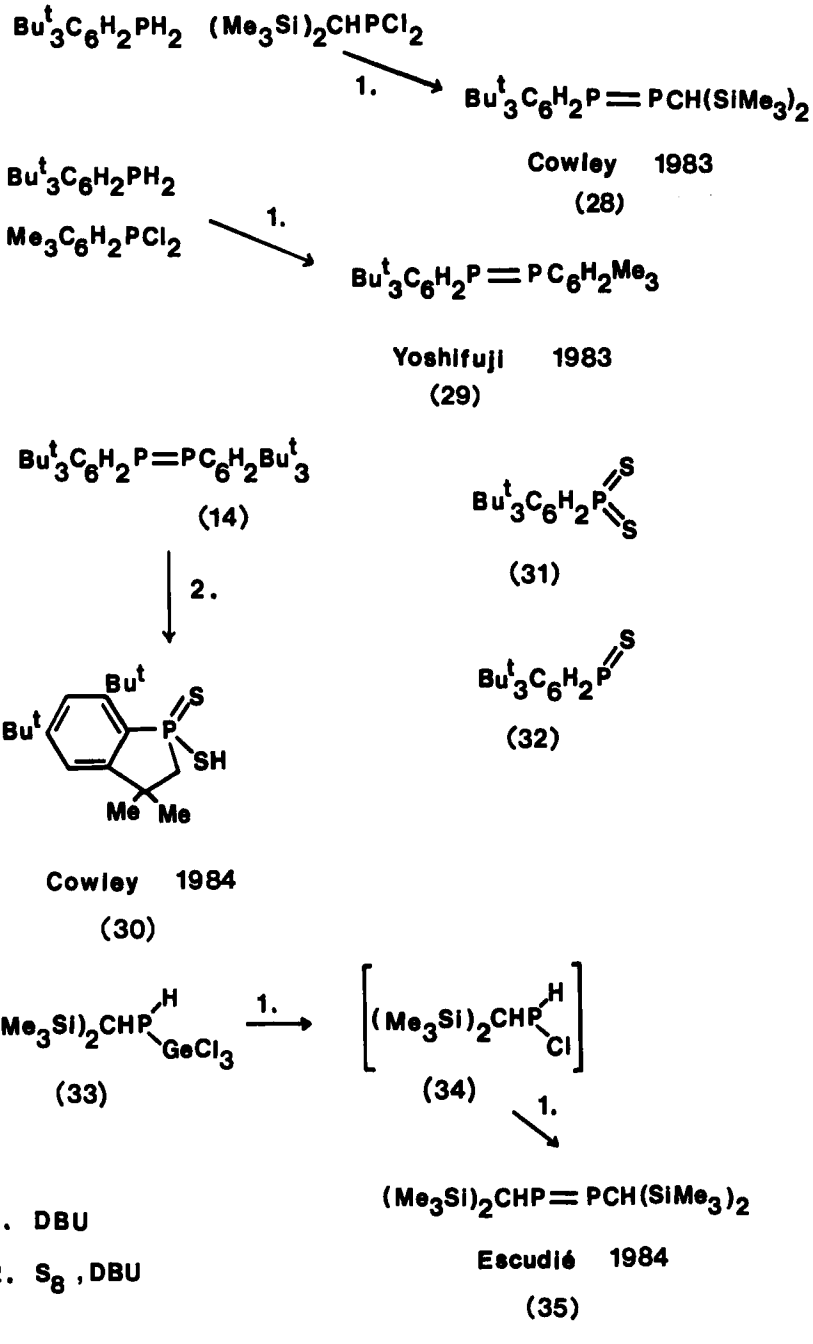
Cowley's group also demonstrated nucleophilic attack on the P=P bond[48] and were able to isolate[49] a novel product of the reaction of (14) with sulphur. The novel P=P bond cleavage product, dithiophosphinic acid (30), was postulated to arise via intramolecular C-H oxidative addition of an ortho-tert-butyl group of (31) or (32).

Escudié has recently developed[50] a route to diphosphenes which are less highly stabilised, unobtainable by other routes, and so amenable to a study of the reactions of the P=P bond. The germylphosphine (33) is used as a precursor to the unstable chlorophosphine (34) which may be intermolecularly dehydrochlorinated to diphosphene (35). (35) could not be prepared by the Cowley method but may be isolated here by distillation and is stable at room temperature for several days.

The structure of Yoshifuji's diphosphene as originally determined[31] exhibits, like all known diphosphenes, a trans



(1) (Me$_3$Si)$_3$ Si Li
(2) PCl$_3$
(3) Bu^t Li
(4) Na Naphthalenide
(5) Me$_3$Si (Bu^t) N Li
(6) PCl$_3$
(7) Li Al H$_4$
(8) Et$_3$ N

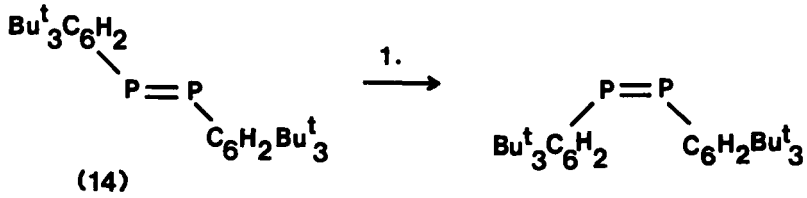


configuration (as well as considerable P=P double bond character). Evidence[51] has now been reported by Koenig, 1984 for the formation of unstable cis-diphosphene (36). Thus laser irradiation of (14) at -78°C resulted in production of the more hindered (36) which reverts to (14) at 0°C. The low activation free energy of the reverse reaction (20.3 kcal mol^{-1}) coupled with the lower energy of (14) are sufficient for the diphosphene to exist almost exclusively in the trans form at room temperature.

Koenig and Escudié, 1984 have studied[52] the ozonolysis of diphosphene (23) and have isolated a stable cyclic diperoxide of structure (37). (37) reacts slowly with methanol at 80°C to give a monoester. The behaviour of (23) is in contrast to the reaction of Yoshifuji's diphosphene (14) with ozone which was reported at the Nice Conference[53] to produce metaphosphonate oligomers (38).

The synthesis and chemistry of diphosphenes has thus been thoroughly investigated over the last five years. The reactions, both electrophilic and nucleophilic, of the P=P double bond will prove to have useful synthetic applications in organophosphorus chemistry. Mention must finally be made of the many diphosphene-organometallic complexes which have been reviewed[54] by Scherer, 1985. Examples of the different modes of coordination are given in the slide.

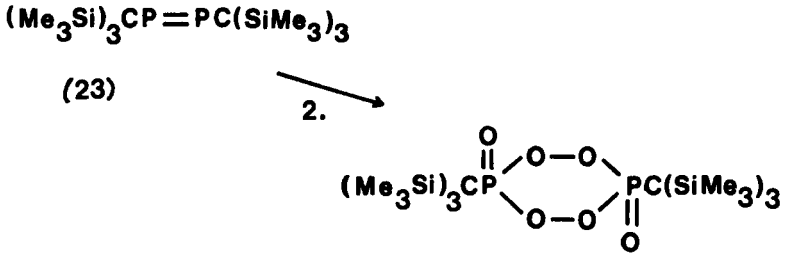
Classical side-on coordination of diphosphenes has been known for the longest time. Complex (39) prepared[55] by Green in 1974 was proposed to contain tetrahedral phosphorus, although an X-ray structure was not determined. This complex provides a model for diimine complexes, proposed as intermediates in nitrogen fixation. Complex (40) prepared[56] by Huttner, 1983 contains coordination both side-on and 2e donation from phosphorus lone-pairs. When (40) is heated[56] at 70°C, binuclear complex (41) is obtained in which the P=P is no longer stabilised by the metal centre. (41) is the first stable derivative of an unstable diphosphene in which only the n-electron pairs are complexed. (42), prepared[57] by Power, is a



(14)

Koenig 1984

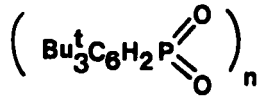
(36)



(23)

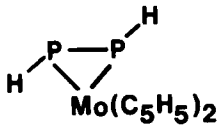
Escudié , Koenig 1984

(37)



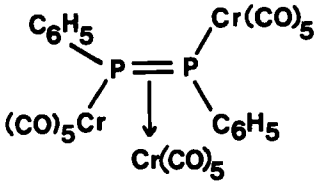
(38)

1. hν 2. O_3



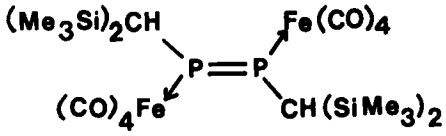
Green 1974

(39)



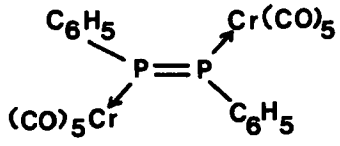
Huttner 1983

(40)



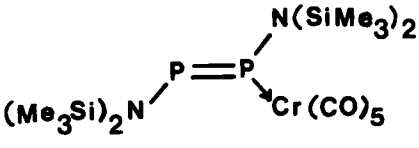
Power 1983

(42)



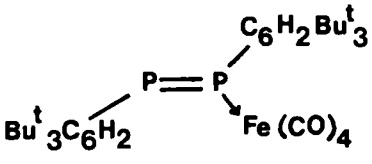
Huttner 1983

(41)



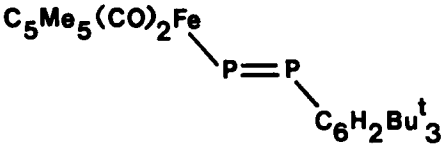
Power 1983

(43)



Cowley 1983

(44)



Weber 1985

(45)

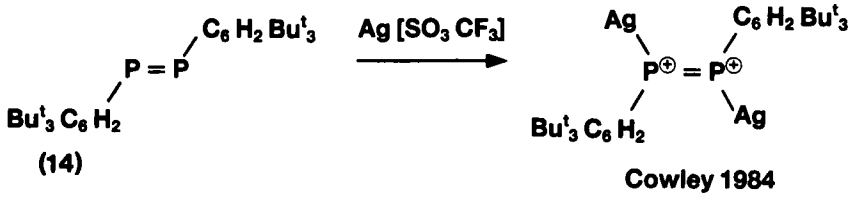
further example of this novel coordination mode. Complexes (43)[58] and (44) represent a further coordination mode. (44), synthesised[59] by Cowley, 1983, contains a highly stabilised P=P but complexation to phosphorus is possible with a small metal moiety in direct reaction of the diphosphene with, for example, $Fe_2(CO)_9$. Weber, 1985 has recently reported[60] the first complexes where one of the groups directly bound to phosphorus is replaced by a metal. In (45) the ligand functions as a 1e donor.

The study of metal complexes of P=P compounds, although fascinating in its own right, has helped to advance the chemistry of diphosphenes. Such work has allowed the preparation of unstable diphosphenes in complex form and enabled their chemistry to be studied. Novel products, unavailable by other routes, can thus be prepared. Recently Cowley, 1984 has prepared[61] the dication (46) by reaction of Yoshifuji's diphosphene with $Ag[SO_3CF_3]$. The structure was demonstrated by ^{31}P and ^{1}H NMR spectra. Dication (47) is isovalent with ethylene and would be a useful molecule to study. Protonation of diphosphenes, however, destroys the P=P double bond, so dication (46), in which $Ag^{\oplus}$ is isolobal with $H^{\oplus}$, is a good model for (47).

Hexaphosphabenzene (48), unlike the stable P_4, has never been prepared and must represent one of the ultimate P=P compounds. Hegarty, 1986 has performed[62] molecular orbital calculations and suggests that (48) might be detected in an inert matrix at low temperatures. (48) is predicted to lie 6 kcal mol^{-1} above free $3P_2$ fragments and to decompose to the latter with an energy barrier of 13 kcal mol^{-1}. Using metal complexation, Scherer, 1985 has prepared[63] a stable compound (49) containing (48) as central bridge-ligand. The P_6 ring is planar and, through ring current effect, shifts the ^{1}H NMR resonances of the methyl groups upfield. Further approaches to (48) are anticipated in the near future.

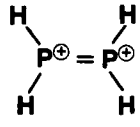
P=X Compounds

The new field of P=P compounds was reviewed in detail. However, two-coordinate P^{III} compounds to other elements are also well-

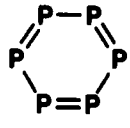


(14)

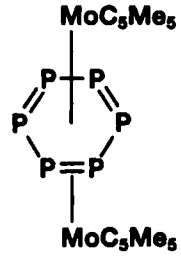
Cowley 1984
(46)



(47)



Hegarty, Nguyen 1986
(48)

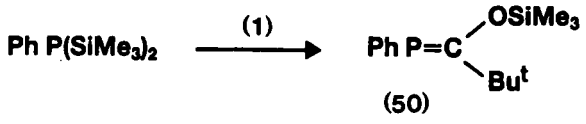


Scherer *et al* 1985
(49)

known. Compounds containing P=C double bonds were prepared first 17 years before the first P=P compound and the chemistry of these molecules has been well explored. The first isolable P=C compound containing a localised bond was prepared[64] by Becker in 1976 during his studies on acylphosphines. Reaction of a disilylated phosphine with a carboxylic acid chloride gave, for example, (50) by initial condensation followed by irreversible silyl group migration. The formation of the strong silicon-oxygen bond is a powerful driving force for this reaction and evidence has also been presented[65] for an N→O migration involving the P=O bond (51). The synthesis and reactions of phosphaalkenes have been recently reviewed by Becker[66] and Appel[67]. Unlike the P=P double bond, which undergoes nucleophilic and electrophilic attack, the major reaction mode of the P=C double bond is of the cycloaddition type. An excellent review[68] of these reactions by Arbuzov has just been published.

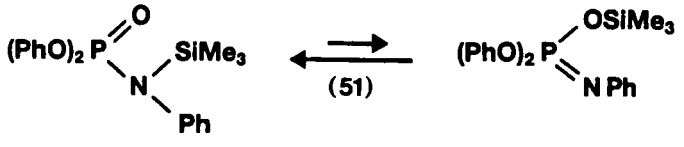
P=N double bonded compounds such as (6) have also been known for some time. A new approach to the preparation of these structures was reported[69] by Markovski, 1983 who found that lithium amides would allow transamination. (52), the first thermally stable dicoordinated C-P=N compound was prepared by this route. This technique has now been extended[70] to the preparation of aminomethylenephosphines via trialkylsilyl migration as in the synthesis of (53).

Development of the monoarylphosphine-alkyl/arylphosphonous dichloride-base route to diphosphenes by Cowley and Yoshifuji has now allowed entry into a variety of novel series with phosphorus multiply bound to heavier main-group elements. In 1983, Cowley prepared[71] and determined crystal structures of the first phosphaarsene (54) and the first phosphastibene (55). Phosphaarsene (54) definitely contains a P=As double bond. The phosphastibene (55) exhibits the lowest-field ^{31}P NMR resonance so far reported (δ 620.0 ppm). It is unstable in solution and decomposes to diphosphene presumably via free phosphinidene. Cowley was unable to prepare phosphabismuthene (56) by this route. Escudié

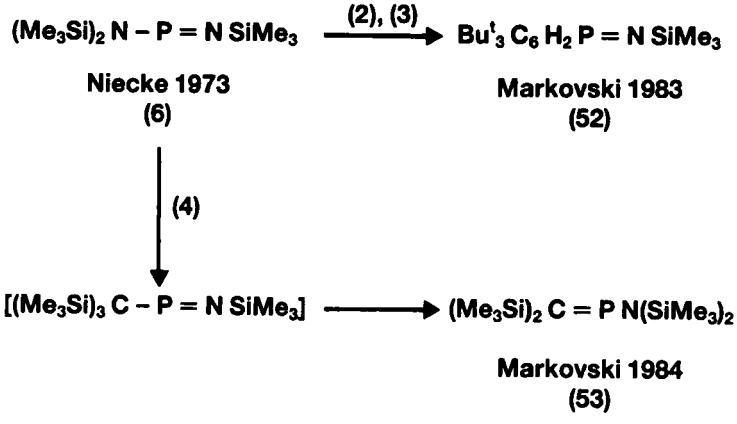


(50)

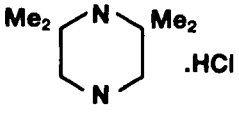
Becker 1976



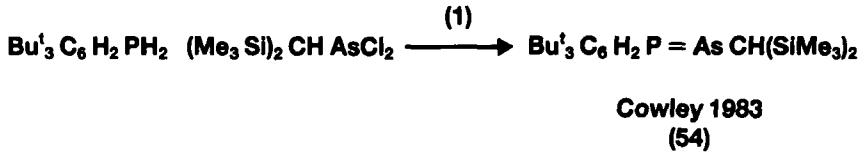
Hodgson, Zon 1976



(1) $Bu^t CO Cl$
(2) $Bu^t_3 C_6 H_2 Li$
(3)



(4) $Li C(SiMe_3)_3$



Cowley 1983
(54)

Bu$^t_3$ C$_6$ H$_2$ P = Sb CH(SiMe$_3$)$_2$

Cowley 1983
(55)

Bu$^t_3$ C$_6$ H$_2$ P = Bi CH(SiMe$_3$)$_2$
(56)

(Me$_3$Si)$_3$ CP = As C(SiMe$_3$)$_3$

Escudié 1983
(57)

Bu$^t_3$ C$_6$ H$_2$ P = Ge(C$_6$ H$_2$ Me$_3$)$_2$

Escudié 1985
(58)

Bu$^t_3$ C$_6$ H$_2$ P = Sn(CH(SiMe$_3$)$_2$)$_2$

Escudié 1985
(59)

Bu$^t_3$ C$_6$ H$_2$ P = Si(C$_6$ H$_2$ Me$_3$)$_2$

Bickelhaupt 1984
(60)

Bu$^t_3$ C$_6$ H$_2$ P(H) – Si(OMe)(C$_6$ H$_2$ Me$_3$)$_2$
(61)

R$_3$ C$_6$ H$_2$ P = O
(62)

R$_3$ C$_6$ H$_2$ P = S
(63)

(1) DBU
(2) MeOH

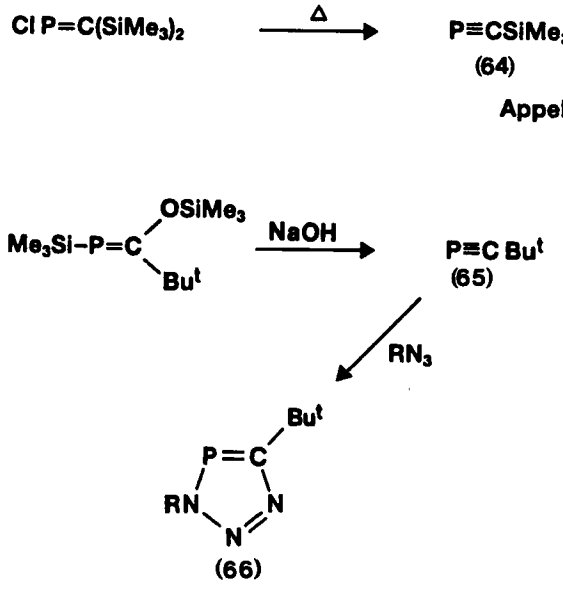
independently synthesised[72] a stable phosphaarsene (57) by coupling a dichlorophosphine with a dichloroarsine using tert-butyllithium and has recently prepared[73] the first stable compound containing a P=Ge double bond (58) and the first stable stannaphosphene (59)[74]. Phosphasilaalkene (60) has been prepared[75] by Bickelhaupt's group although isolation in pure form has not yet been achieved. In all cases (54) - (60), the phosphorus atom is the more negative partner of the double bond, and additions of nucleophiles such as methanol occurs with initial attack at the metalloid centre. All compounds are highly reactive. For example[75], (61) is rapidly formed by treatment of (60) with methanol at room temperature.

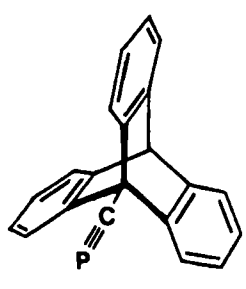
Two members of this series of compounds, (62) and (63), have as yet not been isolated and reports of their synthesis are awaited with interest.

P≡X Compounds

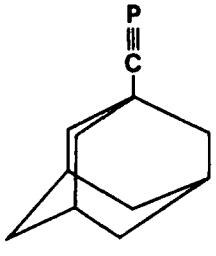
The synthesis and properties of the phosphaalkynes have been collected in the excellent review[67] by Appel. The first members of this series with stability at room temperature were (64) prepared[76] by Appel and (65) prepared[77] by Becker, both by silyl elimination from the phosphaalkenes. (65) has been shown by the groups of Regitz and Carrié, 1984 to possess a wide and interesting cycloaddition chemistry as do the phosphaalkenes. For example, reaction with azides yields[78] the 3H-1,2,3,4-triazaphospholes (66). This cycloaddition chemistry indicates that phosphaalkynes are much closer in behaviour to acetylenes than nitriles, as with the phosphaalkenes, which resemble alkenes more than imines. The latest phosphaalkynes to be prepared are (67), the first crystalline, stable phosphaalkyne of Märkl[79] and adamant-1-ylmethylidynephosphine (68), prepared by Regitz, 1986[80]. The latter phosphaalkyne is also reported[80] to undergo a number of [3+2]cycloaddition reactions with 1,3-dipoles.

By contrast, the chemistry of triply-bonded P^V compounds is virtually unexplored. One transient λ^5-phosphaacetylene (69) has been described[81] (Appel, 1981) and Bertrand, 1985 has recently

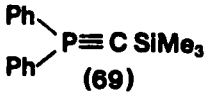




Märkl, Sejpka 1985
(67)

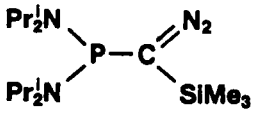


Regitz *et al* 1986
(68)



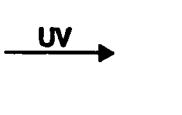
(69)

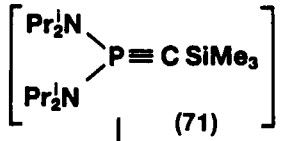
Appel *et al* 1981



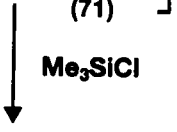
Bertrand *et al* 1985

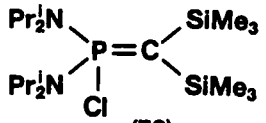
(70)



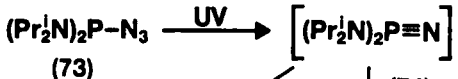


(71)



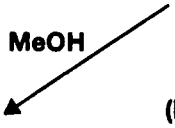


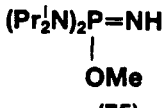
(72)



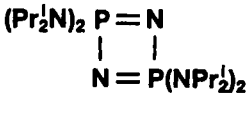
(73)

(74)





(75)



(76)

Bertrand, Majoral *et al* 1984

demonstrated[82] that λ^3-phosphinocarbenes behave as polarised λ^5-phosphaacetylenes. For example, irradiation[82] of (70) in the presence of chlorotrimethylsilane gave (72) in almost quantitative yield. As carbene-trapping experiments were unsuccessful, the formation of product (72) was rationalised in terms of addition to phosphaacetylene-phosphorus vinyl ylide intermediate (71).

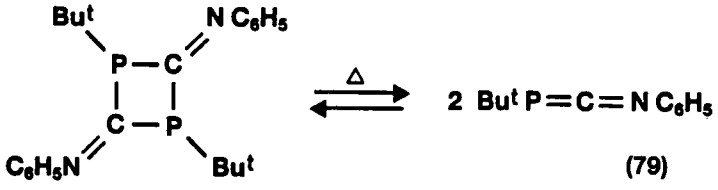
Bertrand and Majoral, 1984 have also demonstrated[83] that the λ^3-phosphinonitrene, formed by photolysis of azide (73), is best represented as nitrilo-λ^5-phosphane (74), by virtue of quantitative formation of addition products such as (75) and a lack of nitrene addition products to olefins. Further proof for the existence of (74) lies in the formation[84] of the first stable cyclodiphosphazene (76) when the photolysis of (73) is carried out in the absence of trapping agents. Bertrand and Majoral speculate[85] that a transient ^{31}P NMR signal at +246 ppm could in fact result from intermediate (74).

P=X=Y Compounds

The last four years have seen a rapid growth in the number of heterocumulenes containing a two-coordinate phosphorus atom since the first stable example (77) was prepared[86] by Kolodiazhnyi in 1982. (77) was shown to react by addition of nucleophiles or by cycloaddition at the P=C double bond. The preparative route for this and subsequent heterocumulenes involves siloxane or silyl halide elimination. Wentrup, 1983 used[87] a similar eliminative approach to the P=C=N system but could only isolate dimer products. Flash vacuum pyrolysis of these dimers such as (78) was used, however, to regenerate monomeric (iminomethylidene)phosphine (79), which was unstable above -25°C.

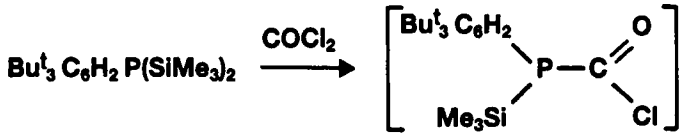
The first phosphaketene (80) was prepared[88] by Appel, 1983 who went on to synthesise[89] the first phosphaketene stable at room temperature (81) by application of a bulky tri-tert-butylphenyl substituent. Once again, the preparative method involved elimination of chlorotrimethylsilane (from (82)). Chemical properties of (80) with respect to addition across the P=C are

$Bu^tP{=}C{=}N\,Bu^t$ (77) Kolodiazhnyi 1982



(78) (79)

Wentrup *et al* 1983



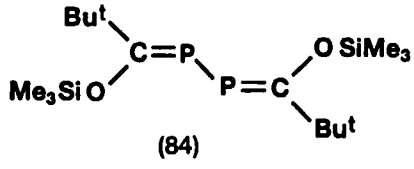
(82)

Appel, Paulen 1983

$Bu^tP{=}C{=}O$ $Bu^t_3C_6H_2P{=}C{=}O$ (81)

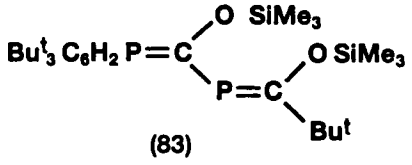
Appel 1983 (80)

$Me_3Si\,P{=}C(O\,SiMe_3)\,Bu^t$



(84)

Appel *et al* 1983



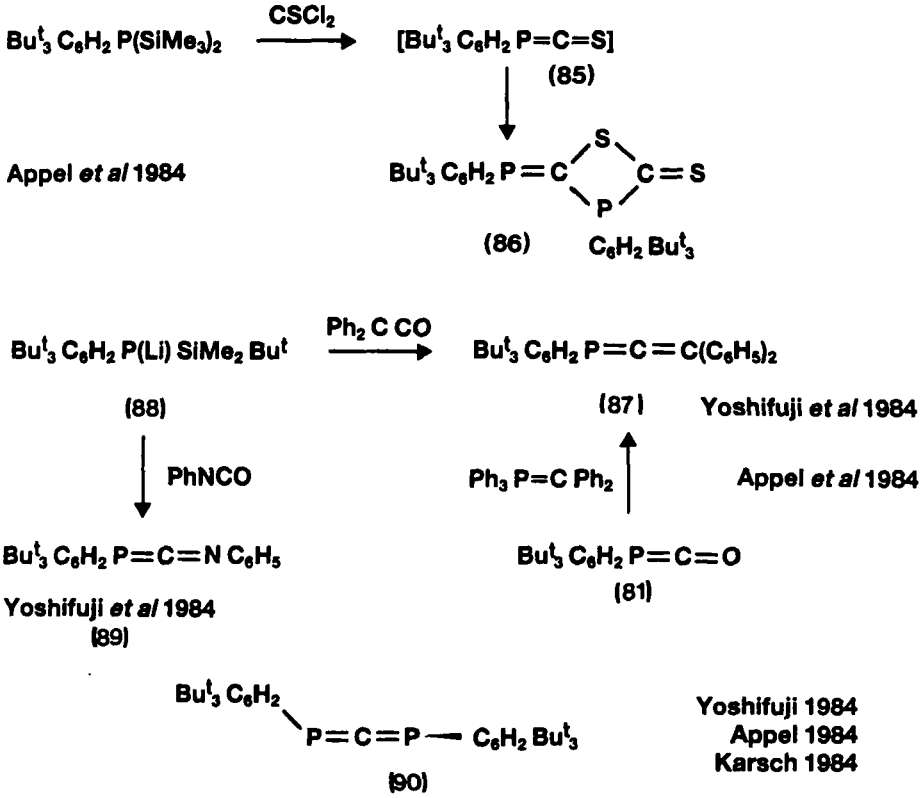
(83)

Appel *et al* 1986

similar to those of isocyanates. Appel, 1986 has most recently used[90] phosphaketene (81) to prepare the first stable acyclic 1,3-diphosphabutadiene (83). Appel had already prepared[91] the stable 2,3-diphosphabutadiene (84) but was unable to prepare the less hindered 1,3- and 1,4-systems similar to (84) owing to rapid internal cycloaddition. The application of such phosphabutadienes in Diels-Alder reactions for the preparation of new heterocycles is awaited with interest. Appel, 1984 has also been able to demonstrate[92] the probable existence of an intermediate phosphathioketene (85) in an analogous reaction to that in which he was able to prepare and isolate phosphaketene (81). Although (85) could not be isolated, its presence was inferred from the isolated dimer (86), formed in an unsymmetrical [2+2]-cycloaddition, a behaviour similar to that of ketenes. The very reactive (85) could be regenerated from (86) by photolysis and trapped with nucleophiles by addition across the C=S double bond.

A number of phosphaallenes have recently been prepared and isolated. Yoshifuji, 1984 has prepared[93] the 1-phosphaallene (87) as a stable crystalline solid by addition of lithiophosphine (88) to diphenylketene followed by siloxane elimination. (87) was reported to be extremely stable to heat, light, moisture and oxygen. Interestingly, (88) also reacted[93] with phenyl isocyanate to give (iminomethylene)phosphine (89), a second example of this heterocumulene type which is stable at room temperature. Appel, 1984 has subsequently reported[94] an independent synthesis of (87) using the phosphaketene (81) by a variation of the Wittig reaction.

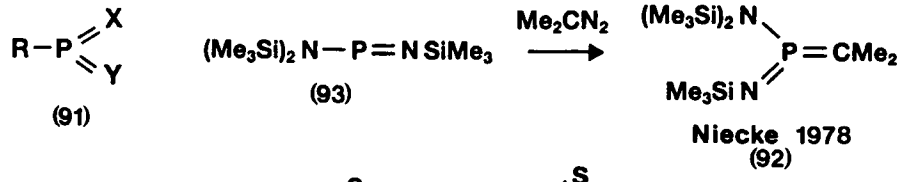
Finally, diphosphaallene (90) has been prepared independently by three groups. Yoshifuji[95] and Appel[94] used lithium silanolate elimination and Karsch[96] eliminated lithium chloride. (90) is once again stable to air and moisture at room temperature and structure determination by Karsch[97] indicates a characteristic heteroallene system with shortened P=C bonds and orthogonal P-substituents.

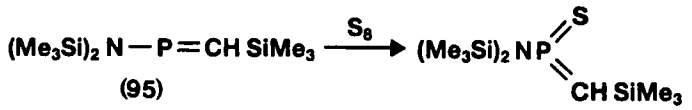


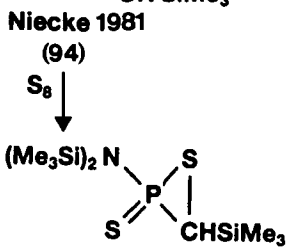
P(=X)(=Y) Compounds

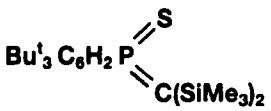
The area of tricoordinated P^V compounds has been transformed, from a study of transient intermediates, into a whole new branch of organophosphorus chemistry dealing with stable molecules within the last five years. Characterisation of the majority of possible molecules (91) has, with some important exceptions, been achieved and it is to be anticipated that the chemical reactions of these compounds will shortly be reported in full. Phosphoranes (91) will now be discussed in detail in four divisions, (91) $Y=CR_2$, NR, O, S.

Niecke, 1978 first reported[98] the isolation of stable iminomethylenephosphoranes such as (92). They were prepared by reaction of iminophosphane (93) with α-alkylated diazoalkanes. The extra stabilisation afforded by the α-alkyl group results in inhibition of [2+2] and [2+1] cycloadditions. The same researchers similarly reacted (95) with sulphur and isolated[99] methylenethioxophosphorane (94). (94) was isolated as a water-sensitive liquid which readily reacted[99] with an excess of sulphur to give the novel heterocycle (96). More recently Appel[100], 1984 and Neilson and Watson[101], 1984 have isolated crystalline methylenethioxophosphoranes (97) and (98) by a similar reaction. The latter group reported[101] the crystal structure of (98) and confirmed the sp^2 bonding at phosphorus. Mathey, 1984 has reported[102] a study of the cycloaddition reactions of methylene-phosphine sulphides. His approach is to synthesise stable precursors of the more reactive unsubstituted methylenephosphine sulphides which on thermolysis could generate the latter at reasonable temperatures and their reactivity could then be studied with various trapping agents. Thus thermolysis of (99) at 110°C in the presence of 2,3-dimethylbutadiene led to Diels-Alder adduct (100). This novel Diels-Alder reaction of (101) is noteworthy in that such a cycloaddition has not been observed with methylenephosphine oxides and could reflect a difference in reactivity between the P=C double bonds in these two systems. Mention here should be made of the careful study[103] by Bickelhaupt,

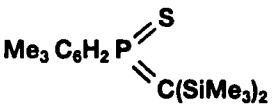




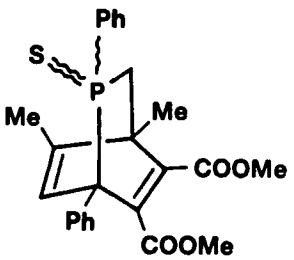




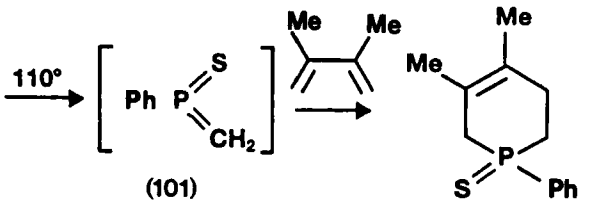
Appel and Casser 1984
(97)



Neilson, Watson 1984
(98)



(99)



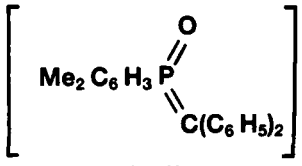
Mathey, Deschamps 1984
(100)

1983 of the reactions of the oxidation products of phosphaalkenes with nucleophiles. Although intermediate methyleneoxophosphorane (102) and methylenethioxophosphorane (103) were not isolated, their presence was inferred by the isolation of alcohol addition products (104) and (105) across the P=C double bonds.

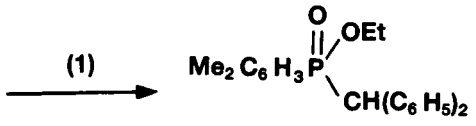
The first stable methyleneoxophosphorane (106) has now been isolated[104] by Appel, 1984 in crystalline form. The structure was confirmed by X-ray analysis. This same group of workers were also the first to isolate[105] bis(methylene)phosphoranes such as (107). X-ray structure analysis was performed. Stable examples of methylenephosphoranes (108) are thus complete. Appel, 1985 has most recently prepared[106] the first stable tris(methylene)phosphate ion (109). The X-ray crystal structure of the tetra(tetrahydrofuran)-coordinated lithium salt of (109) confirms the presence of the planar PC_3 grouping, identical CPC bond angles and three P=C double bonds.

Similar to (108), the iminophosphorane series (110) is represented by all of the possible structures in stable form. The key syntheses of (9) by Niecke[26] and Scherer[27], 1974 and of (11) by Scherer[28], 1974, which may be regarded as seminal to this exciting field, have already been mentioned. Metaphosphonimidate (111) was shown[107] by Bertrand and Majoral, 1980 to be a transient intermediate formed by photolysis of diphenylphosphine azide. Dimerisation and addition of nucleophiles across the P=N double bond were the characteristic reactions. Markovski, 1984 has now reported[108] the first examples of sterically protected stable metaphosphonimidates (112) formed by reaction of an iminophosphine with ozone or sulphur.

The most interesting and elusive of the 3-coordinate P^V compounds are those in which phosphorus is doubly-bound to two oxygen atoms (113). An excellent review of the field has been presented[109] by Westheimer. The structures (113) derive their major importance because monomeric metaphosphate (114) is implicated in one of the two major mechanisms of phosphate ester

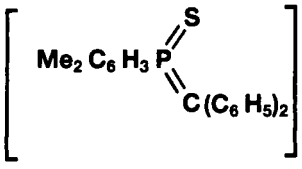


(102)

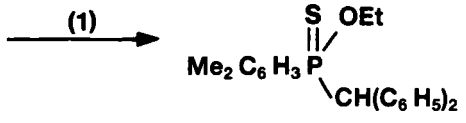


(104)

Bickelhaupt 1983



(103)



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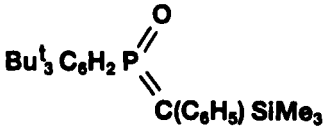
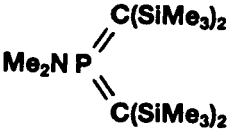


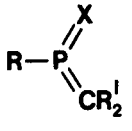
Appel *et al* 1984

(106)



Appel *et al* 1982

(107)



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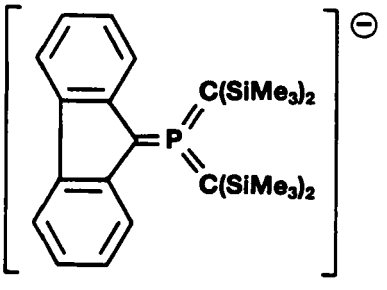
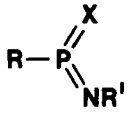


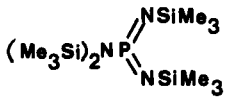
Appel *et al* 1985

(109)



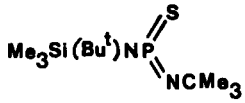
(110)

(1) EtOH



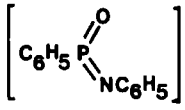
Niecke , Scherer 1974

(9)



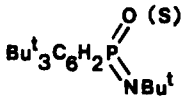
Scherer 1974

(11)



Bertrand , Majoral 1980

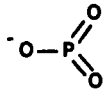
(111)



Markovski 1984

(112)

(113)



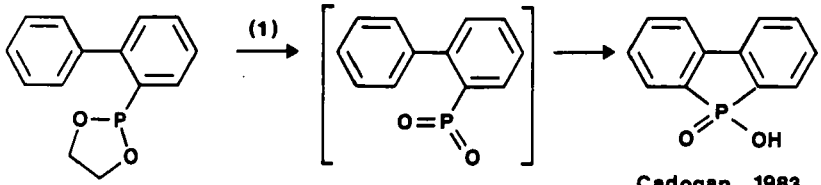
Meyerson , Hass , Ramirez 1984

(114)

$\Delta H_f^o (PO_3^-)$ -190 kcal/mol

$\Delta H^o (HPO_3 \rightarrow H^+ + PO_3^-)$ 314 kcal/mol

Henchman , Freedman 1985



(115)

(117)

Cadogan 1983

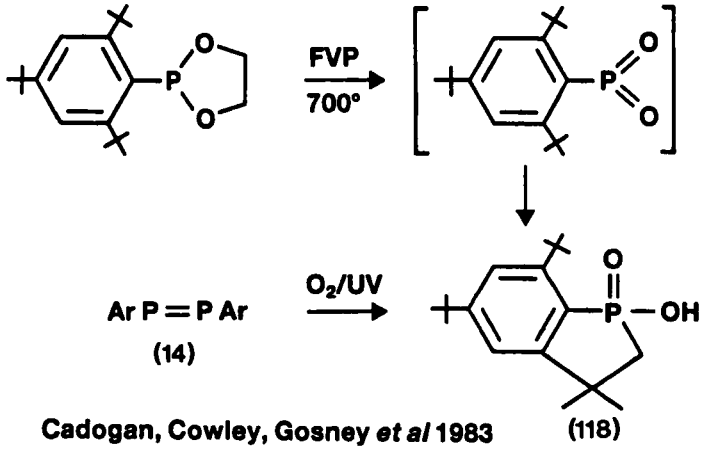
(116)

(1) 600-800°C

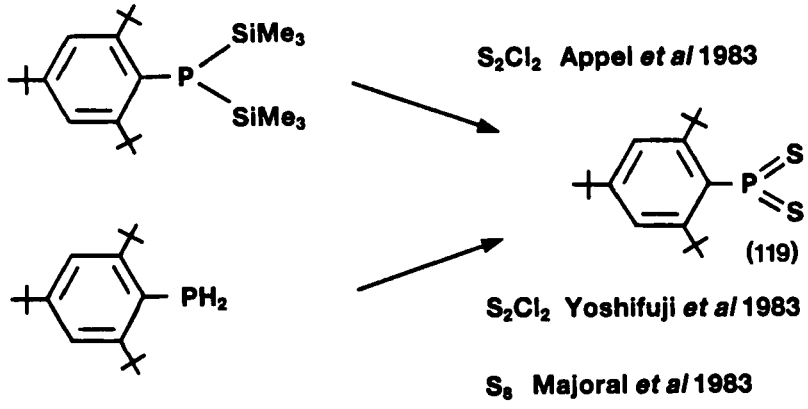
hydrolysis. Recent advances in the aqueous solution chemistry of (114) will be reviewed in a later section. In contrast to in aqueous solution, metaphosphate (114) has been observed free in the gas phase. Meyerson, Hass and Ramirez, 1984 report[110] the results of a detailed study of the formation and decomposition of monomeric metaphosphate anion generated by negative-ion chemical-ionisation mass spectroscopy of phosphotriesters. The major pathway to (114) involves electron capture, loss of vinyl or aryl group to produce dimethyl phosphate anion and elimination of dimethyl ether. (114) can decompose further to yield metaphosphite anion. Henchman, 1985 reports[111] experimental measurements of some thermodynamic and kinetic properties of (114). Studies of phosphate-doped plasmas set heat of formation of (114) at -190 kcal mol^{-1}. (114) is more stable than NO_3^-. Heat of deprotonation of HPO_3 is 314 kcal mol^{-1}, so that this is the strongest acid and consequently (114) is the weakest base. (114) has also been shown[111] to be unreactive towards acids, electrophiles and nucleophiles when generated in a gas flow reactor. This behaviour is in distinct contrast to the behaviour of hydrated (114).

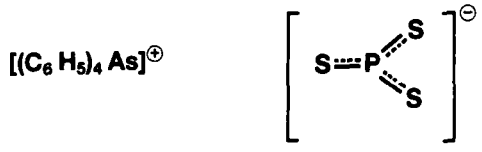
Cadogan and Gosney, 1983 have reported[112] the unambiguous trapping of a metaphosphonate species for the first time by an intramolecular insertion reaction. Previous evidence for their detection is tenuous because intermolecularly trapped products could also have derived from metaphosphonate oligomers. Flash vacuum pyrolysis of (115) at 600 - 800°C gave almost quantitatively (116), the anticipated product of intramolecular trapping of monomeric (117) by an adjacent phenyl group. This reaction necessitates the intermediacy of the strongly electrophilic monomeric metaphosphonate. Cadogan's group also have reported[113] the first example of the insertion of PO_2 intramolecularly into an alkyl C-H bond. The product (118) is also produced by the novel photooxidation of Yoshifuji's diphosphene (14).

Dithioxophosphorane (119) is a stable solid which has recently been prepared by Appel[114], Yoshifuji[115] and Majoral[116], 1983. X-



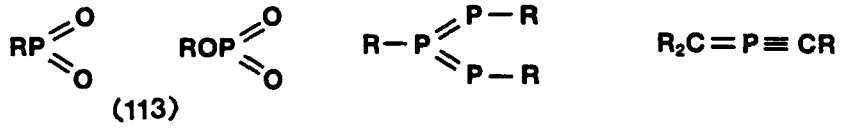
Cadogan, Cowley, Gosney *et al* 1983 (118)



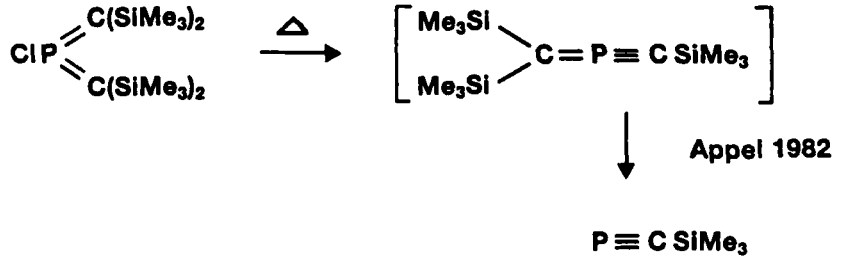


Roesky, Ahlrichs 1986

(120)



(113)



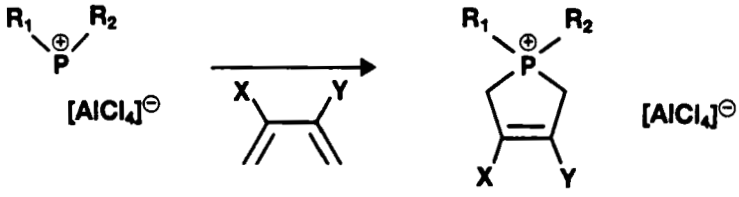
ray diffraction analysis demonstrated planarity of the CPS_2 moiety and nucleophilic addition and cycloaddition reactions of the P=S double bond were performed. Most recently, Roesky and Ahlrichs, 1986 have prepared[117] the sulphur analogue of monomeric metaphosphate anion as a stable solid salt. Tetraphenylarsonium trithiometaphosphate (120) was shown by X-ray structure analysis to contain a monomeric pyramidal anion.

We have seen how the majority of tricoordinated P^V compounds have now been synthesised in stable form. Such products are available for the development of reactions and applications of these new organophosphorus compounds. Further work is still required, however, to determine the physical and chemical properties of the as yet unisolated metaphosph(on)ates (113). Of the many possible new compounds awaiting synthesis two heterocumulenes may be cited. Interestingly, Appel, 1982 has proposed[118] the phosphaeneyne as an intermediate in the gas-phase thermolysis of a chlorobis(methylene)phosphorane. It is quite certain that we shall see more exciting developments in this area in the years to come.

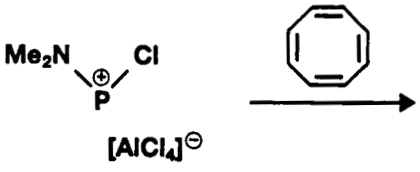
NEW SYNTHESES OF ORGANOPHOSPHORUS COMPOUNDS

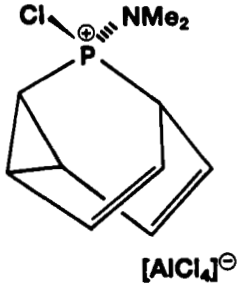
Phosphenium Ions

A comprehensive review of the preparation and properties of two-coordinate phosphorus cations, phosphenium ions, by Cowley has appeared[119]. As electrophilic carbenoids, phosphenium ions react with 1,3-dienes and this has proved to be their most interesting and preparatively useful reaction mode. Independently, Baxter[120] and Cowley[121], 1983 reported 1,4-addition to give a series of 3-phospholenium tetrachloroaluminates. A concerted [2+4] addition mechanism is preferred[121] because reaction with trans-2-trans-4-hexadiene is highly stereospecific. Baxter and Cowley, 1986 have reacted[122] a phosphenium ion with cyclooctatetraene to prepare 9-phosphabarbaralane (121). The first structural information on a

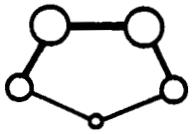


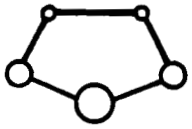
Baxter, Cowley 1983



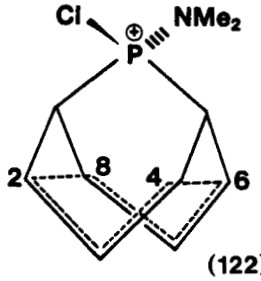


Baxter, Cowley 1986
(121)





Schaefer 1985
(123)



(122)

hetero-atom substituted barbaralane was obtained and the geometry of this molecule was shown to approach the geometry of the transition state for a Cope rearrangement. Although substitution of semibullvalenes has produced long C_2 - C_8 bonds and short C_4 - C_6 distances, X-ray structural determination of (121) revealed that these distances are extremely close and represents the closest approach to a bishomoaromatic system (122) yet reported.

A theoretical study by Schaefer, 1985 on the phosphocenium ion has revealed[123] that the most stable structure is represented by (123) with the two rings adopting a point-to-edge conformation and phosphorus bound via P-C single and P-C_2 three-centre to the two rings respectively. It is anticipated that further work on the synthesis of this elusive molecule will be encouraged by this study.

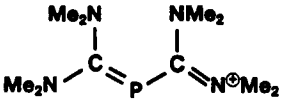
Phosphonium Ions

The work of Schmidpeter on the chemistry of the triphosphorus cations such as (124) continues to appear. The X-ray crystal structure of (124), synthesised by reaction of triphenylphosphine, phosphorus trichloride and aluminium chloride, indicates[124] average P-P distance between that of PP single and double bonds and a small PPP angle. Protonation of the central phosphorus atom has now been shown[125], Schmidpeter, 1985 to result in a complete loss of this π-bonding between phosphorus atoms. The X-ray crystal structure of (125) indicates normal pyramidal coordination of the central phosphorus atom. This situation is paralleled by the 2-phosphaallyl cations which are best represented[126] by the structure shown for (126). Methylation of (126) involves binding of the π-electron pair on phosphorus and loss of the conjugated allylic system giving structure (127).

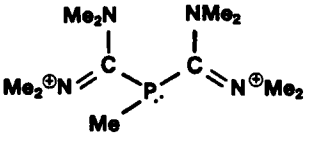
Schmutzler, 1985 has performed[127] the double quaternisation of two directly-bonded phosphorus atoms. The preparation of (128) is of theoretical interest as it was hoped to achieve a P- P single bond length different from the standard of 220 pm. X-ray crystal

Schmidpeter *et al* 1985
(124)

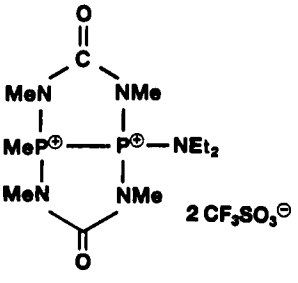
Schmidpeter 1985
(125)



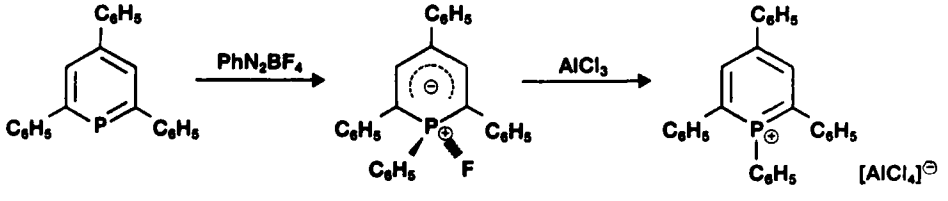
Schmidpeter *et al* 1985
(126)



Schmidpeter *et al* 1985
(127)



Schmutzler 1985
(128)

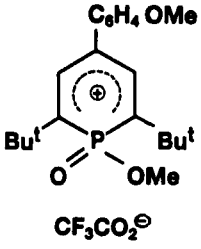


(130) (131) Dimroth 1984 (129)

structure analysis, however, showed this bond length to be similar to others at 218.9 pm. All of the P-N bonds, however, are shortened, especially that to the NEt_2 group, indicating strong multiple bonding enabling delocalisation of the positive charge over nitrogen.

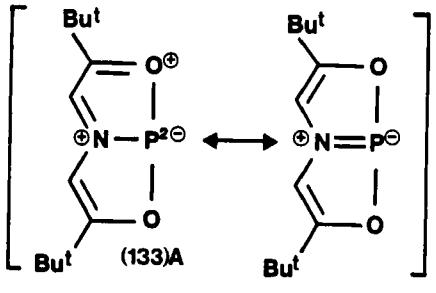
The first synthesis of a stable, crystalline phosphininium salt (analogous to the pyridinium salts) with three carbon residues bonded to the phosphorus, (129) has been reported[128] by Dimroth, 1984. Treatment of phosphinine (130) with phenyldiazonium tetrafluoroborate had been shown to give λ^5-phosphinine (131) which could be reacted with aluminium chloride to give (129). (129) is extremely reactive, reverting to λ^5-phosphinine derivatives such as (131) with nucleophiles. The high electrophilicity of (129) indicates very little electron flow from the 6π-system to the $P^{\oplus}$-centre. Dimroth, 1984 has also prepared[129] the highly reactive carbocation system (132) in which stabilisation of the unfavourable α-phosphinyl carbonium ions is achieved by delocalisation.

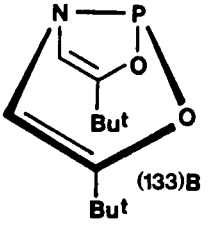
A final compound in which phosphorus is present in an unusual bonding state is the first phosphorandiide (133) synthesised[130] by Arduengo, 1984. This compound, prepared by reaction of phosphorus trichloride with an aminodiketone is free to choose between the 10-P-3 bonding scheme of (133)A or the 8-P-3 system of (133)B. X-ray crystal structure determination indicates a planar geometry consistent with (133)A. This illustrates the considerable stability of the 10-electron bonding system at phosphorus. The 10-P-3 system of (133)A can be reorganised[131] to normal bonding (133)B by complexation with platinum. Single-crystal X-ray structure determination of complex (134) reveals the folded (133)B structure with localised π-bonds. Complexation of the 10-P-3 system is unfavourable on steric grounds and because of the low p-orbital character of the lone pairs on phosphorus. Decomplexation of (134) at -50°C gives 10-P-3 system only.



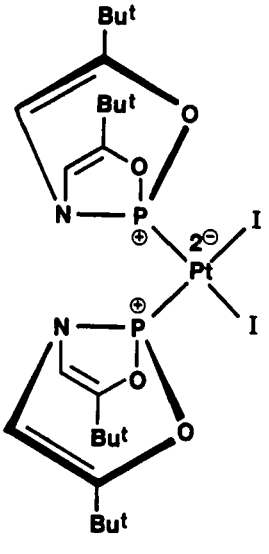
Dimroth *et al* 1984

(132)





Arduengo,1984



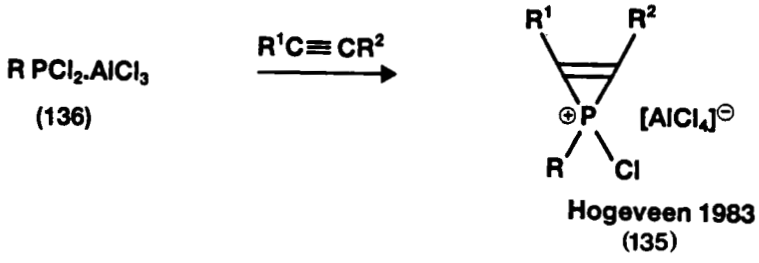
Arduengo,1986

(134)

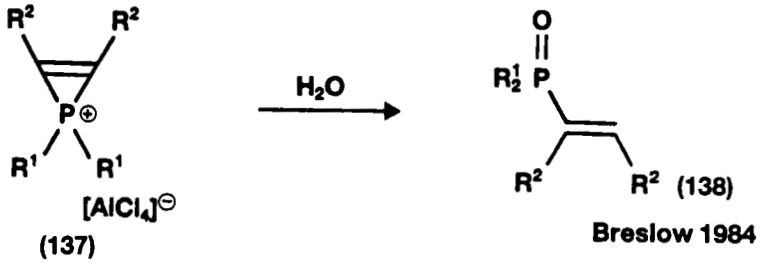
Small-Ring Compounds

The first phosphirenium salts (135) have been reported by Hogeveen, 1983 who reacted[132] the adduct of dichlorophosphines with aluminium chloride (136) with acetylenes. Transient phosphenium ions could be involved in these reactions. Breslow has since extended[133] this reaction to chlorodialkylphosphines and has prepared the stable phosphirenium salts (137). All react rapidly with water to give phosphine oxides (138). Theoretical interest attaches to phosphirenium cations because of the possibility of three-orbital, two-electron delocalisation. Mathey, who reported[134] the first unambiguous synthesis of the phosphirene ring (as a stable metal complex), has now been able to report[135] the first synthesis of a free tervalent phosphirene (139) by decomplexation of metal complex (140). (139) is surprisingly stable, given that X-ray crystal structure determination indicates no C=C double bond delocalisation to phosphorus and a very strained ring. Mathey's group has since reported[136] the chemical reactions of complexed and free phosphirenes with electrophiles, nucleophiles and dienes. The most exciting of these reactions is the preparation[137], in complexed form, of the unknown phosphorus-analogues of azetinones (141) by the first carbonylation of a C-P bond.

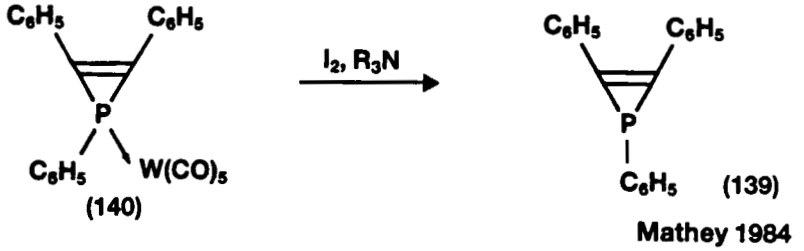
The bulky substituent approach to the stabilisation of reactive phosphorus compounds continues to find application to the preparation of ever more unusual small-ring compounds. The first stable, non-complexed and non-carbon substituted diphosphirane (142) has been prepared[138] by Koenig, 1986 by the addition of diazomethane to Yoshifuji's diphosphene (14). (142) does not dimerise on heating. Baudler's group continues to explore the chemistry of organocyclophosphanes and has succeeded[139] in linking two P_3 ring skeletons via a σ-bond (143). Fluck, 1985 has prepared[140] a derivative of the simplest bicyclic phosphane, P_4H_2 (144) by the opening of only one bond of the P_4 tetrahedron of phosphorus with tri-tert-butylphenyllithium. Yoshifuji, 1985 has developed[141] a new route to very stable phosphiranes by reaction of



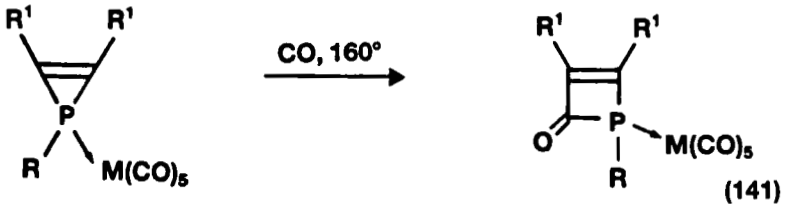
Hogeveen 1983
(135)



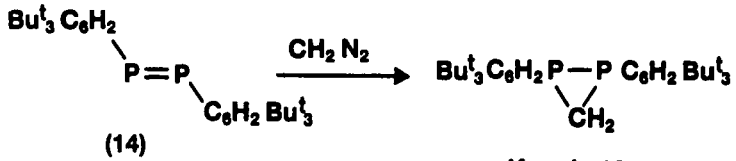
Breslow 1984



Mathey 1984



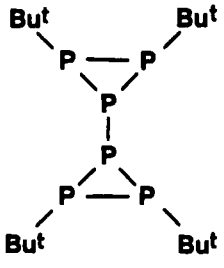
Mathey 1985



(14)

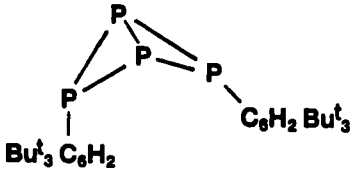
Koenig 1986

(142)



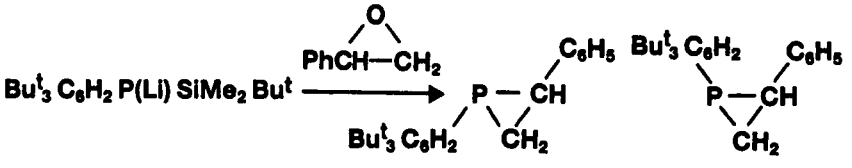
Baudler 1984

(143)



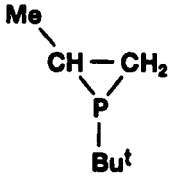
Fluck 1985

(144)



Yoshifuji 1985

(145)



Baudler 1985

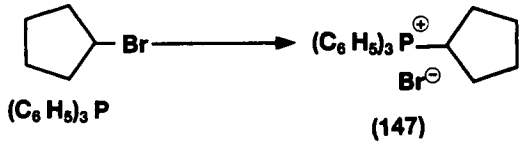
(146)

a phosphine with an epoxide assisted by a silyl group. A mixture of E- and Z-isomers of (145) were obtained. Monophosphirane (146), stable despite the low degree of substitution, has been prepared[142] by Baudler's group, 1985.

New Preparative Techniques

Dauben and co-workers have applied their studies of reactions at high pressure to the preparation of Wittig phosphonium salts with great effect[143]. The utility of the Wittig reaction is sometimes reduced if labile functional groups or stereochemically sensitive centres are present, as salt formation is generally performed at 80 - 140°C. Now, under conditions of high pressure, it is possible to prepare alkyltriphenylphosphonium halides in good yields at room temperature. Dauben's results with secondary alkyl bromides, which react poorly in S_N2 displacements, are illustrative. Cyclopentyl bromide requires a temperature of 200°C to react with triphenylphosphine to produce 43% of (147) at atmospheric pressure. At 15 kbar pressure, high yields of (147) can be achieved at 20°C. It is anticipated that this new mild method for quaternisation of phosphines will find synthetic application in the preparation of sensitive olefins.

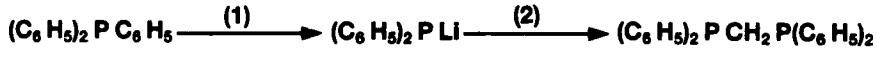
Tertiary phosphines are generally prepared by the reaction of an alkyl halide with a dialkylphosphide anion. The latter are most conveniently prepared by treatment of the readily available phenylphosphines with lithium. This heterogeneous reaction is, however, time-consuming, especially on large scales. Chou, 1985 has now been able[144] to dramatically increase reaction rates by the application of ultrasound. For example, rate of preparation of (148) is increased x30 by ultrasonication on a 5 g scale. This reaction which leads to important chelating ligands such as (149) is now much improved.



Dauben 1984

(147)

Solvent	Time	Temp	Pressure	Yield
$C_6H_6 : MeC_6H_5$	24h	20°C	15 k bar	11%
MeCN	36h	20°C	15 k bar	52%
MeCN-Excess Halide	36h	20°C	15 k bar	79%
MeCN	36h	20°C	1 bar	0%
None	12h	200°C	1 bar	43%



82%
Chou 1985

(148)

(149)

(1) Li, 720 min or Li, Ultrasound, 25 min, 25°C
(2) $BrCH_2Br$, 0°C

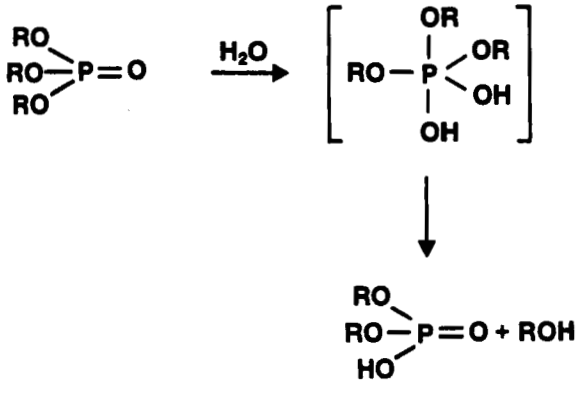
EXPLORATION OF REACTION MECHANISMS IN ORGANOPHOSPHORUS CHEMISTRY

Hydrolysis of Phosphate Esters - Monomeric Metaphosphate

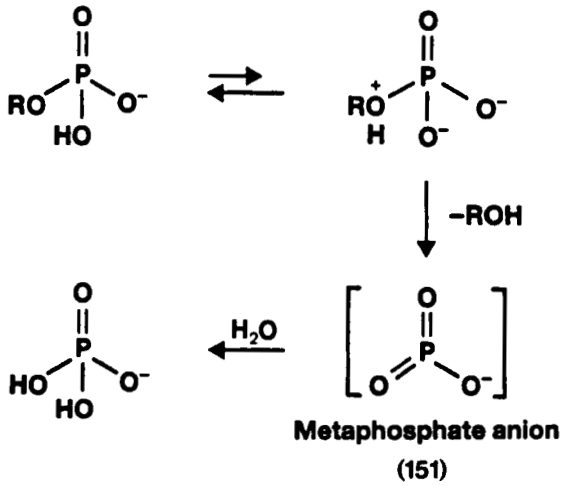
Phosphate ester hydrolysis is one of the most important and complex of the reactions involving phosphorus. Of the many detailed mechanistic pathways that may be followed, two extreme cases give a useful summary; that in which the coordination number at phosphorus is increased (150) and the second involving the intermediacy of metaphosphate (151). Westheimer has reviewed[109] his own important contributions, together with the literature to 1981, to the understanding of the details of this second mechanism, and the evidence, mainly kinetic, for the intermediacy of monomeric metaphosphate, is concisely detailed.

The most important contribution to mechanistic organophosphorus chemistry of the last decade must surely be the independent synthesis of Oxford[145] and Harvard[146], 1978 of chiral phosphate esters (152). The use of these valuable products in the determination of the stereochemical course of a number of chemical and enzyme-catalysed phosphoryl-transfer reactions has recently been reviewed[147] by Lowe, 1983.

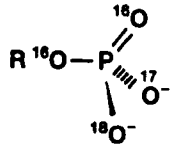
Knowles, 1985 has now used (152) to demonstrate[148] the first case of racemisation at phosphorus during the solvolysis of a phosphoric monoester and therefore provide the first stereochemical evidence for the intermediacy of metaphosphate. Knowles found that phospho group transfer from the dianion of phenyl [(R)-$^{16}O,^{17}O,^{18}O$]phosphate (153) to tert-butanol in acetonitrile occurs with racemisation to give racemic tert-butyl esters (154). This result is consistent with free monomeric metaphosphate with a long enough half-life to lose all stereochemical memory before capture by the hindered nucleophile. However, the authors also conclude[148] that the result is consistent with an alternative interpretation. Thus the phospho group may be transferred to solvent acetonitrile



(150)



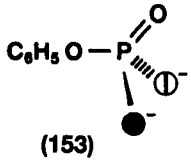
(151)



Lowe, Cullis 1978

Knowles *et al* 1978

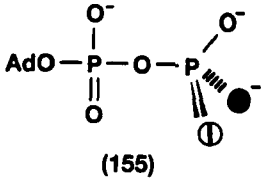
(152)



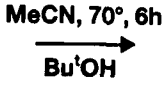
(153)

Knowles, Friedman 1985

(154)



(155)



Racemisation

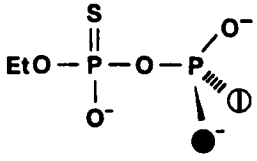
Cullis, Rous 1986

and racemisation may then occur through a sequence of rapid phospho group transfers among acetonitrile molecules before final capture by tert-butanol.

Cullis, 1986 has independently demonstrated[149] that similar solvolysis of adenosine 5′-[β-(S)-^{16}O,^{17}O,^{18}O]diphosphate (155) results in phosphoryl transfer to 2-O-benzyl-(S)-propane-1,2- diol with racemisation. Once again, it is not possible to distinguish between free metaphosphate or a preassociative mechanism involving acetonitrile. However, Cullis's observation[150] of a 70% racemisation pathway for phosphoryl transfer from P^1-O-ethyl-P^1-thio[P^2-^{16}O,^{17}O,^{18}O]pyrophosphate (156) to 2-O-benzyl-(S)-propane-1,2-diol in dichloromethane as solvent provides more persuasive evidence for a relatively free metaphosphate in this reaction medium which is less likely to participate in phosphoryl transfer than acetonitrile.

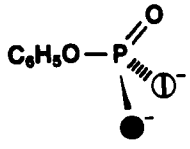
The third situation, the transfer of phosphoryl in protic solvents, has also received the benefit of stereochemical probing. Knowles, 1984 has demonstrated[151] that methanolysis of phenyl [(R)-^{16}O,^{17}O,^{18}O]phosphate (153) and 2,4-dinitrophenyl [(R)-^{16}O,^{17}O,^{18}O]phosphate (157) proceed with complete inversion of configuration at phosphorus. Such displacements must therefore occur by preassociative mechanisms in which bond breaking dominates the rate-limiting process. Knowles' results cannot distinguish between preassociative concerted (loose S_N2- like transition state) or preassociative stepwise (metaphosphate intermediate of extremely short life-time) reaction pathways.

This important series of stereochemical studies strongly suggests that in water and alcohols, the metaphosphate is never free and is only formed productively when the nucleophile is preassociated with it. Ramirez, 1986 has recently determined[152] the volume of activation, $\Delta V^{\neq}$ for the hydrolysis of 2,4-dinitrophenyl phosphate dianion (158) to be -4.8 cm^3/mol. The fact that this reaction is accelerated by pressure rules out a bond cleavage liberating free metaphosphate. The situation in weakly

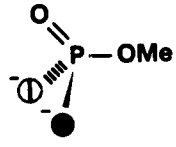


(156)

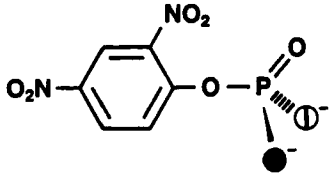
(1) → 70% Racemisation
Cullis, Rous 1985



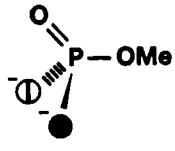
(153)

(2) → 

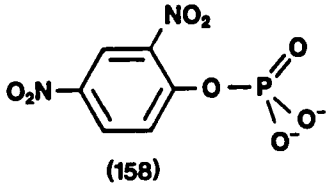
Knowles *et al* 1984



(157)

(3) → 

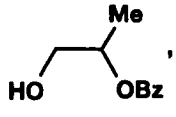
Knowles 1984



(158)

(4) → $\Delta V^{\ddagger}$ −4.8cm^3/mol

Ramirez *et al* 1986

(1) CH_2Cl_2, Me I,  , 25°C

(2) MeOH : H_2O, pH 4.7, 100°C

(3) MeOH : H_2O, pH 10.2, 22°C

(4) H_2O, pH 12, 43.2°C

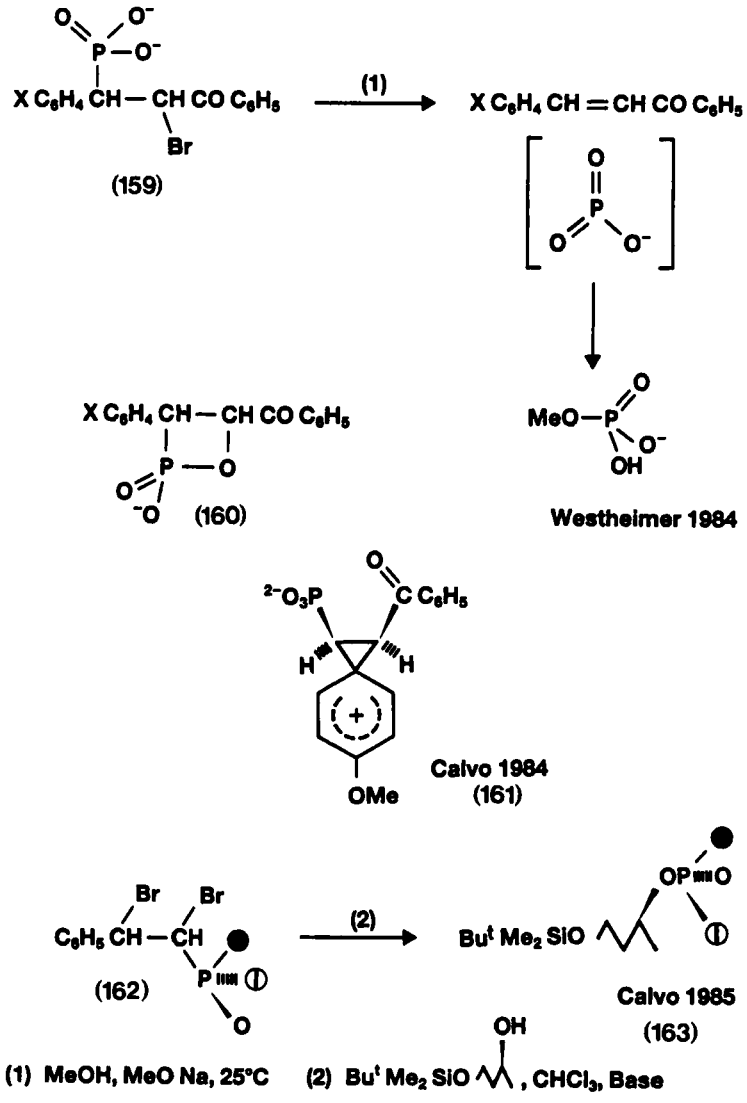
nucleophilic aprotic solvents is less clear. The stereochemical results are not inconsistent with free metaphosphate, although this reactive intermediate, which will complex even with weak nucleophiles, probably exists in bound form.

Conant-Swan Fragmentation

An early example of the Conant-Swan fragmentation of β-halophosphonates is the production of tert-butyl phosphate when 2-chlorooctylphosphonate decomposes in the presence of tert-butanol. The early evidence in favour of a free metaphosphate ion as intermediate in this reaction has been reviewed[109] by Westheimer, 1981. Westheimer, 1984 and Calvo, 1984 have now probed more deeply into the mechanism of this fascinating reaction using modern techniques. Westheimer, 1984 studied[153] the decomposition of β-halophosphonates (159) at 25°C and concluded that the reaction appears to be a simple fragmentation involving free monomeric metaphosphate. Westheimer's conclusion was reached from the following experimental results.

- Rate of decomposition of dianion is greater than that of the monoanion by 10^4. This is inconsistent with a process of displacement at phosphorus.
- Rate of decomposition is unaffected by additional nucleophiles.
- Solvent isotope effect is absent indicating a lack of nucleophilic assistance.
- 25-fold rate increase by substitution of p-methoxyl group into the first phenyl of (159) indicates that formation of the double bond occurs in the rate limiting step. A phostone intermediate (160) is ruled out by this and further data.

Westheimer finally makes the point that the metaphosphate may be regarded as free as it arises without nucleophilic assistance and without significant bond forming to accompany bond breaking. However, the lifetime of this intermediate may be extremely short;

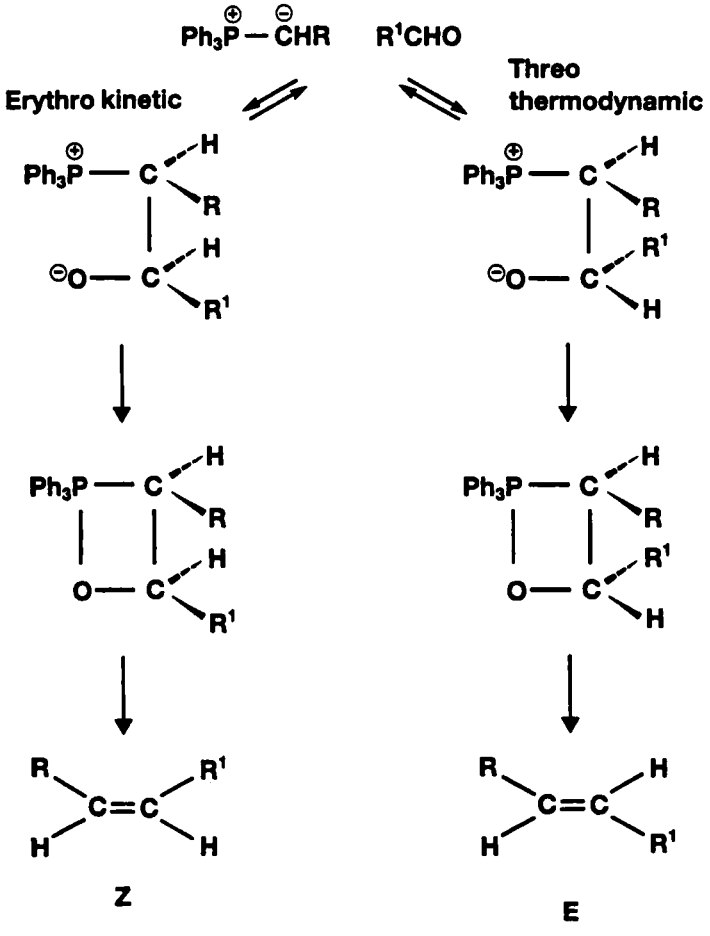


it could not be determined from this study whether free metaphosphate survives collision with nucleophilic solvent.

In an accompanying paper, Calvo presented[154] the result of a stereochemical study to rule out the intermediacy of a phenonium ion intermediate (161) in Conant-Swan fragmentation of p-methoxy-substituted (159). Preparation of pure 1R,2S-enantiomer of (159) (X = p-methoxyl) and fragmentation to E-olefin was described. Its diastereoisomer fragments to the Z-olefin. These facts rule out the intermediacy of a phenonium ion. Finally, Calvo, 1985 has determined[155] the stereochemistry of the phosphate ester formation in the Conant-Swan fragmentation. He found that reaction of (1,2-dibromo-2-phenylethyl)-[(R)-^{16}O,^{17}O,^{18}O]phosphonic acid (162) with 1-[(1,1-dimethylethyl)dimethylsilyloxy]-(S)-butan-3-ol in the presence of base in chloroform produced ester (163) with inversion at phosphorus. This fascinating result parallels Knowles' findings on phosphate ester hydrolysis/alcoholysis which proceeds by a preassociative mechanism in which metaphosphate is never free or has only an extremely short life-time. Calvo makes the interesting point, however, that decreasing the nucleophilicity of the alcohol might be expected to increase the life-time of the proposed metaphosphate and so allow stereochemical racemisation, favoured by Knowles as evidence of true metaphosphate intermediacy, to be realised.

Wittig Reaction

The Wittig olefin synthesis, together with the Horner/Wadsworth-Emmons modification, is one of the more important organic synthesis reactions and it is not surprising, therefore, that it continues to attract the interest of physical organic chemists. Over the last three years, sophisticated crossover and ^{31}P NMR experiments have been applied to map out in more detail the different mechanistic pathways as the stability of the phosphorus ylide is varied. The stage has been reached where phosphorus ylides may now be used under appropriate conditions to produce Z- or E-olefins to >90% selectivity.

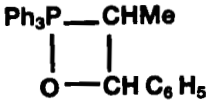


As you are all aware, the reaction scheme in the slide is a useful framework for a discussion of the stereochemistry of the Wittig reaction. Reactive ylides follow the kinetically favoured erythro betaine-oxaphosphetane route and generally produce Z-olefins to >90% selectivity. Stabilised ylides favour the thermodynamic route to E-olefins. Schlosser has used lithium salts to good effect with unstable ylides to favour E-selectivity, possibly by enhancing thermodynamic stability of the threo-betaine LiX adduct[156].

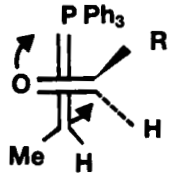
Pioneering work by Vedejs, 1973 had established[157] the oxaphosphetanes as key intermediates by low temperature ^{31}P NMR spectroscopy. The oxaphosphetanes (164) showed two sharp singlets in the proton noise-decoupled spectrum at -5°C, 10 Hz apart at δ + 62.7, corresponding to cis and trans isomers. At -70°C, the temperature at which (164) is stable, resolution was not possible. Failure to detect betaines in such non-stabilised ylide reactions encouraged Vedejs to propose[157] a $\pi 2s + \pi 2a$ cycloaddition to explain Z-selectivity in such cases (165).

Reversible dissociation of the Wittig intermediate into starting ylide and aldehyde is used to explain E-selectivity with the more stabilised ylides. Schlosser, 1967 used[158] a crossover experiment to provide evidence and the ^{31}P NMR study of Vedejs, 1981 corroborated[159] these results. However, crossover could only be observed using oxaphosphetanes prepared from aromatic but not aliphatic aldehydes.

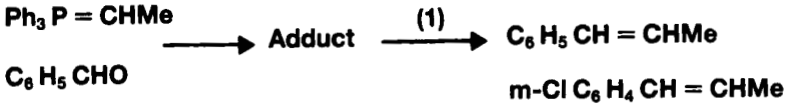
Maryanoff, 1984 has extended[160] the use of ^{31}P NMR spectroscopy to a study of oxaphosphetanes (166) in which the use of the n-propyl group allows the ^{31}P NMR signals of the cis- and trans-oxaphosphetanes to be well separated for quantification and kinetic studies. Maryanoff was able to demonstrate that the original ratio of cis-(166):trans-(166) (3.8:1) did not determine the Z:E olefin ratio 1.5:1. This can be related to cis- to trans-oxaphosphetane conversion during the reaction - thermodynamic control.



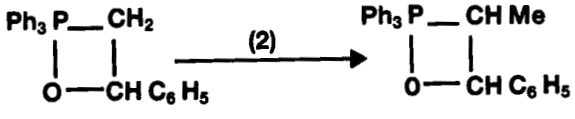
Vedejs 1973
(164)



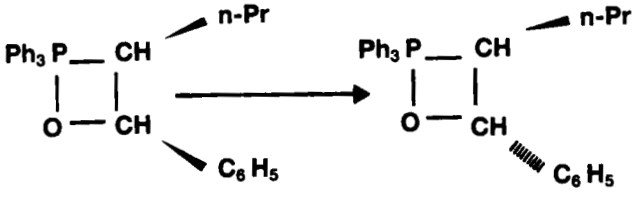
Vedejs 1973
(165)



Schlosser 1967



Vedejs 1981
(164)



Maryanoff 1984
(166)

(1) m-ClC$_6$H$_4$CHO
(2) −24°C, Ph$_3$P= CHMe

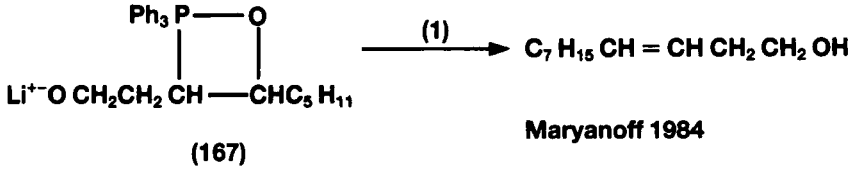
Vedejs could not observe[159] crossover with non-stabilised ylides reacted with aliphatic aldehydes and Maryanoff observed[160] zero stereochemical drift for such a system. However, Maryanoff,1984 has now demonstrated[161] reversibility of oxaphosphetanes (167) derived from hexanal and (γ-oxidopropylidene)triphenylphosphorane by crossover products with octanal. This finding is suggested to account for enhanced E-stereoselectivity in the reaction of γ- and β-oxido ylides with aliphatic aldehydes. Maryanoff, 1985 has now extended[162] his studies to the reaction of ylides, substituted in the side-chain with oxido, carboxylate, amino or amido groups, with aromatic and aliphatic aldehydes. A pattern of enhanced E-stereoselectivity has emerged and is thought to depend upon the ability of anionic groups to facilitate reversibility of oxaphosphetane formation.

Maryanoff, 1985 has most recently[163] noticed synergistic stereochemical drift between diastereomeric oxaphosphetanes (168) and (169) during alkene production. Deprotonation of pure erythro-(170) results in stereochemical drift whereas deprotonation of pure threo-(171) does not. The presence of lithium ions enhances the former. Crossover with m-chlorobenzaldehyde occurs with erythro-(170) but not with threo-(171). Stereochemical drift is enhanced when erythro-(170) is deprotonated in the presence of threo-(171). These results indicate that cis-(168) is much more prone to reversal than trans-(169) and that cis- and trans-oxaphosphetanes interact synergistically to enhance E-alkene formation.

α-Phosphonyl Carbonium Centres

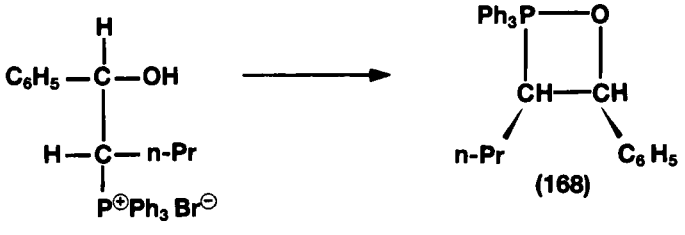
The electron-withdrawing diethyl phosphonate group stabilises carbanions and such anions (172) are used in the Wadsworth-Emmons modification of the Wittig reaction. The effect of this group on the stability of an adjacent carbocation or carbon free radical centre has now been evaluated.

Creary, 1983 had reported[164] the results of his comprehensive study of the solvolysis of mesylates (173) in which product, rate and solvent effect determinations implicate carbocationic



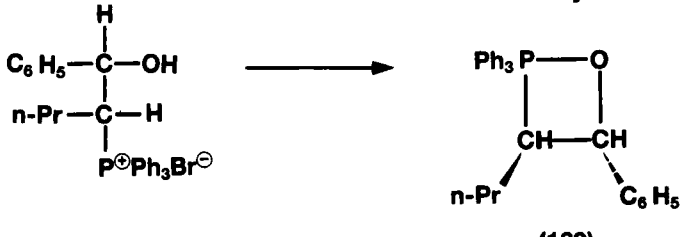
(167)

Maryanoff 1984



(170) (168)

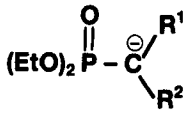
Maryanoff 1985



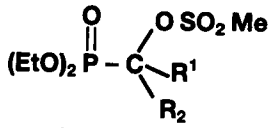
(171) (169)

(1) $C_7H_{15}CHO$

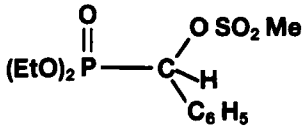
intermediates despite the electron-withdrawing phosphonate substitutent. Mesylate (174) gave exclusive substitution products and optically active (174) gave racemic products on trifluoroacetolysis. α-Deuterium isotope effect rules out significant solvent assistance. These two results argue strongly in favour of a k_c process involving cation (175) as a discrete intermediate. Mesylate (176) gave exclusive elimination and β-deuterium isotope effect together with small m value suggests reversible formation of an ion-pair intermediate-cationic analogue of E1cb mechanism. Determination of σ_p^+ for $PO(OEt)_2$ (0.505) together with the magnitude of solvolysis rates for (174) suggests that the rate-retarding effect of this substituent is unexpectedly small. Creary suggests[164] that a stabilising interaction between the diethyl phosphonate group and the cationic centre involving a 3d orbital on phosphorus (177) must be in operation to explain the unexpected ease of generation of cations adjacent to this highly electron-withdrawing group. Creary, 1985 has extended[165] this study to the series of substituted aryl phosphonates (178). A Hammett ρ value of -10.1 in the electron donor substituent region for trifluoroethanolyses of (178) again points to an offsetting cation stabilising feature for $PO(OEt)_2$ to explain the ease of formation of these cations. The ρ value for solvolysis of benzyl mesylates $XC_6H_4CH_2OSO_2Me$ in hexafluoroisopropanol was -11.6; demand for aryl group stabilisation in the intermediate phosphoryl-substituted cation does not surpass that of the α-H analogues. Pasto, 1985 has reported[166] a timely theoretical study of the interaction of phosphonate groups with a carbocationic centre. Pasto found that methylenephosphonic acid cation (179) is best represented as the cyclic structure on the basis of geometry optimisation calculations. The detailed studies of Creary, however, have not provided any support for the cyclic cationic intermediate. The latest study of Creary, 1986 of the solvolysis of α-thiophosphonyl



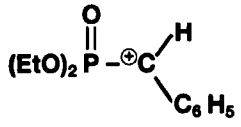
(172)



(173)

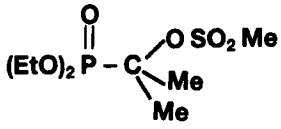


(174)



(175)

Creary 1983



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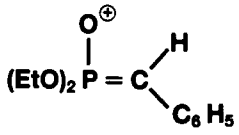
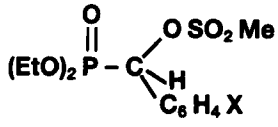
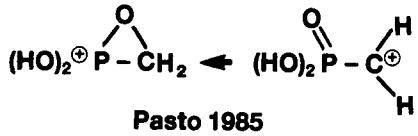


(177)



Creary 1985
(178)



Pasto 1985
(179)

mesylates has provided[167] convincing evidence for a k_Δ process involving thiophosphonyl participation to cyclic intermediate cations (180).

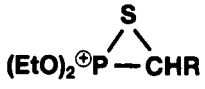
Finally Creary, 1985 has studied[168] the effect of the diethyl phosphonate group on the stabilities of free radicals. The methylene-cyclopropane rearrangement (181) → (182) was chosen to probe this interaction as it is a free radical process devoid of polar character in the transition state. A p-diethyl phosphonate group increases the rate of rearrangement by 1.48 so that this group is free radical stabilising. This stabilising effect is conjugative as m-substitution results in rate retardation. Direct attachment of the diethyl phosphonate group to the cyclopropane ring results in a greater spread of rates (183). Creary suggests that spin delocalisation into vacant phosphorus d-oribtals is responsible for this free radical stabilisation.

In summary, the diethyl phosphonate group is very similar to the carbonyl and cyano groups in that all are carbanion and free radical stabilising and all three interact with carbocationic centres to reduce the destabilising inductive effect.

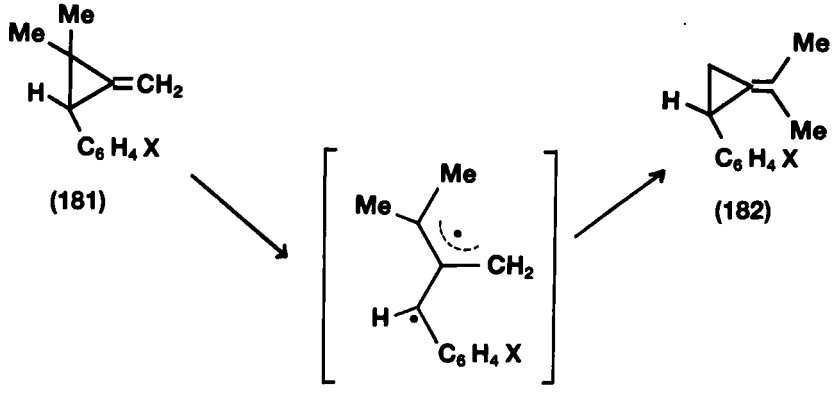
Asymmetric Phosphorus Compounds

In this final section, further examples of the use of asymmetric phosphorus compounds, particularly the chiral phosphate esters of Lowe and Knowles, in the elucidation of the mechanisms of important reactions in organophosphorus chemistry, will be described. A number of the reactions in this section have now been found to proceed stereospecifically and they are therefore finding application in nucleotide chemistry.

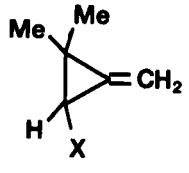
The stereochemistry of the reaction of dialkyl phosphoranilidates with isoamyl nitrite to yield dialkyl hydrogen phosphates has been elucidated[169] by Stec, 1985. Cadogan, 1962 was first to describe the use of nitrosyl chloride for this transformation[170] and since then it has found frequent use in oligonucleotide synthesis. Stec now finds that each



Creary 1986
(180)



(181) (182)



Creary 1985
(183)

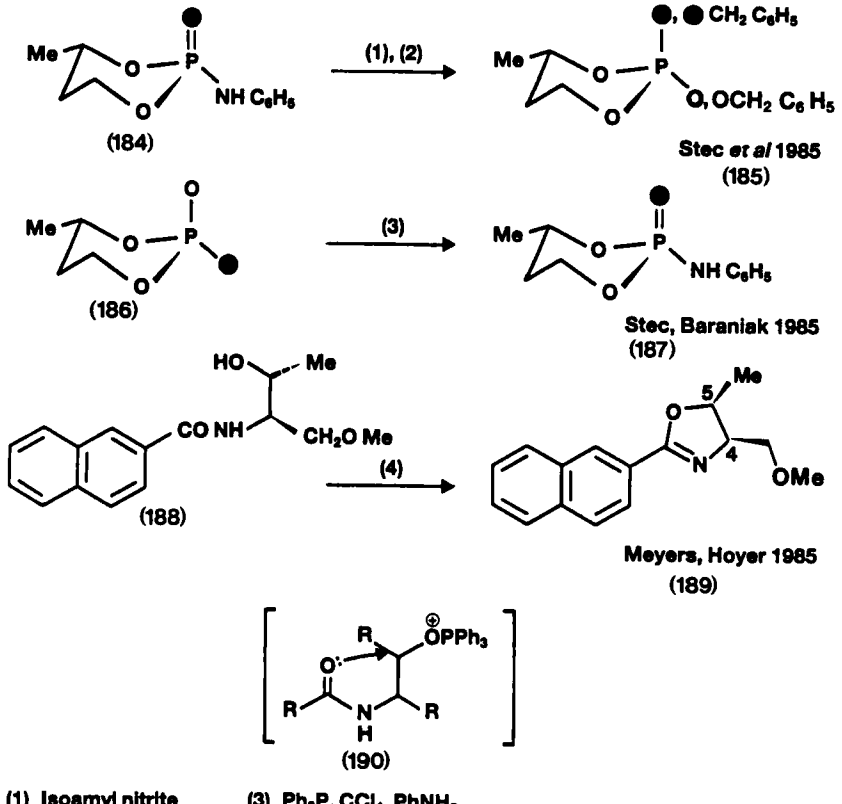
X	k_{rel}
H	1
$(EtO)_2\overset{O}{\overset{\|}{P}}$	32
$EtO\overset{O}{\overset{\|}{C}}$	560

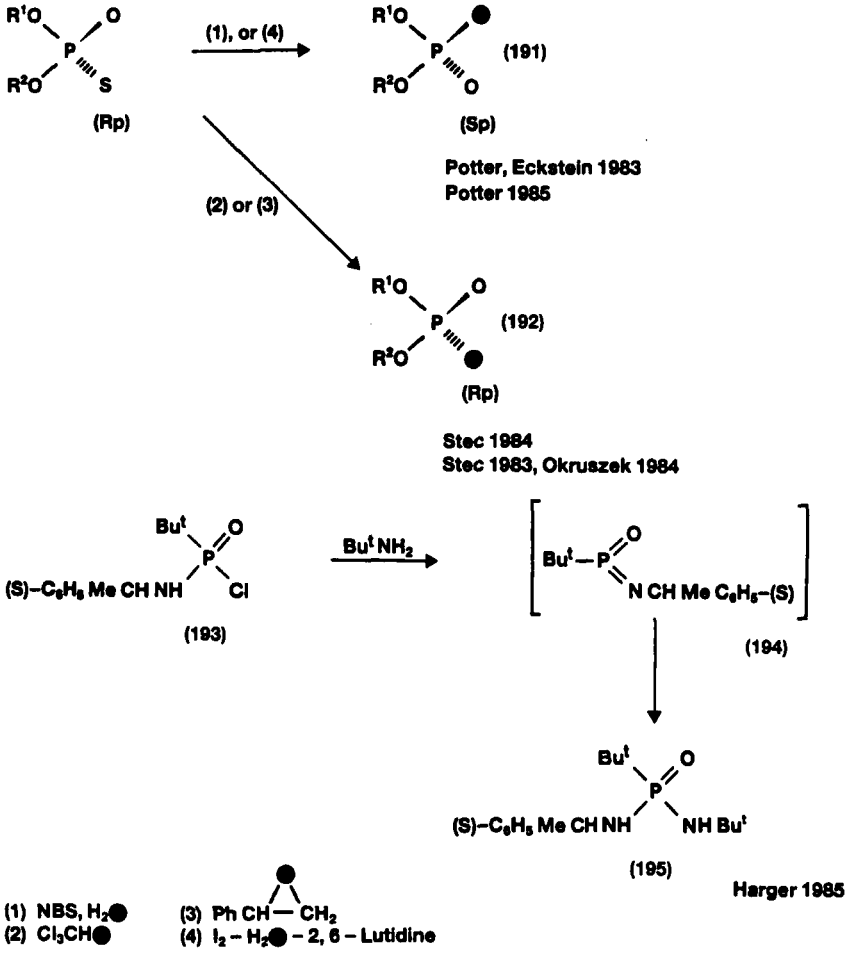
diastereoisomer of (184) is converted with retention of configuration at phosphorus (>95%) into triesters (185).

The mechanism of the reverse reaction, the conversion of dialkyl phosphates into phosphoranilidates by reaction with triphenylphosphine-carbon tetrachloride-aniline described[171] by Appel, 1975 has also been clarified by Stec, 1985. Stec determined[172] the stereochemistry of the conversion of cis-(186) (and its trans-isomer) into phosphoranilidates (187) and observed inversion of configuration. The mechanism involves preponderant activation by Ph_3P-CCl_4 of axial oxygen followed by nucleophilic attack by amine at phosphorus. Meyers, 1985 has shown[173] that the similar conversion of β-hydroxyamides, formed by the Ph_3P-CCl_4 condensation of acids and amino-alcohols, into oxazolines also occurs with inversion at the carbinol centre. The original (R,R)-configuration in (188) was converted into the (4R,5S)-oxazoline (189) by a complete inversion process through intermediate (190).

Optically-active nucleoside phosphorothioates have recently been prepared with a variety of structures and have been used to study the mechanism of action of phosphorolytic enzymes. Considerable effort has recently been devoted to the conversion of these valuable substrates into oxygen chiral phosphates for further enzyme studies. Potter and Eckstein, 1983 performed the first synthesis of a dinucleoside phosphate isotopically chiral at phosphorus. They employed[174] N-bromosuccinimide to oxidatively displace sulphur with inversion (191). Stec, 1984 has now used[175] [^{18}O]chloral to convert dialkyl phosphorothioates into P-chiral [^{18}O]phosphates (192) with retention. [^{18}O]Styrene oxide has been shown[176] to give a similar result in this transformation. Potter, 1985 has demonstrated[177] that iodine in aqueous 2,6-lutidine inverts nucleoside phosphorothioate diesters, whereas in aqueous pyridine epimerisation results.

Finally, an important study by Harger, 1985 has demonstrated[178] the intermediacy of free metaphosphonimidate (194) in the reaction of phosphonamidic chloride (193) with tert-





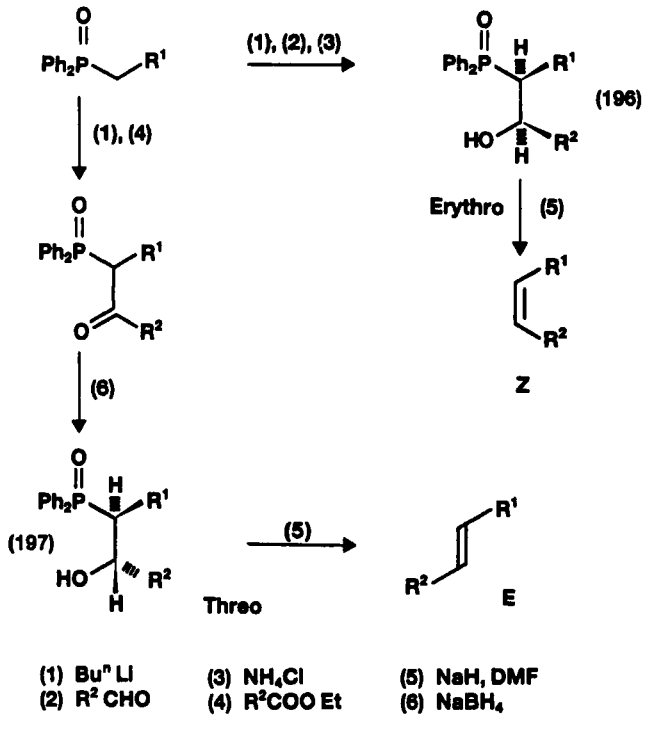
butylamine in highly dilute solution. Thus both diastereoisomers of (193) gave the same mixture (55/45) of the diastereoisomers of product (195). At higher amine concentrations, increasing stereospecificity suggests that the preassociation pathway is becoming more favoured.

APPLICATION OF ORGANOPHOSPHORUS COMPOUNDS TO ORGANIC SYNTHESIS

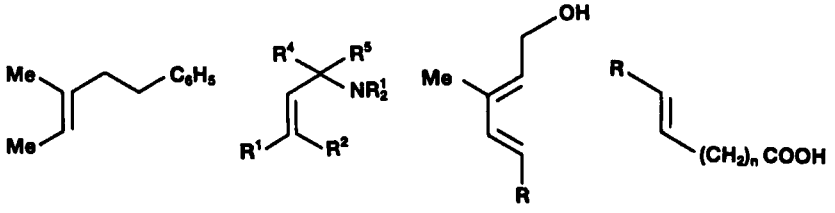
The literature of organic chemistry from the last three years is replete with examples where organophosphorus reagents have played key roles in synthetic transformations. In this final section, brief mention will be made of the important new developments in this area.

Warren, during the period 1981 - 1983, has developed[179] a version of the Horner-Wittig reaction using the diphenylphosphinoyl group which allows 80 - 90% stereoselective synthesis of either erythro (196) or threo (197) intermediates from the same phosphine oxide and almost 100% stereospecific elimination of $Ph_2PO_2^-$ from either to give essentially pure Z- or E-olefin respectively. This reaction sequence is an excellent complement to the Wittig reaction in those cases where stereochemical control is poor. Over the last three years, Warren has continued to explore the scope of this reaction and has prepared both E- and Z- tri-substituted alkenes (198)[180], N- allyl amides (199)[181], α-hydroxydienes (200)[182], unsaturated acids (201)[183], homoallylic alcohols (202)[184] and a number of allylically substituted compounds formed by stereospecific opening of epoxides (203) with nucleophiles[185], the latter having been formed by epoxidation with high stereoselectivity induced by the diphenylphosphinoyl group[186].

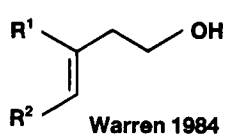
Corey, 1985 has developed[187] a new Wittig reagent for the stereospecific synthesis of 1,3-dienes by cis-olefination of aldehydes. Ylide (204) reacted with hindered aldehyde (205) to give only the Z-olefin (206). This could then be oxidised and heated to produce 1,3-diene (207) by Cope elimination. The more usual Wittig reagent for this transformation, allylidene



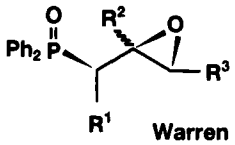
Warren 1981 – 1983



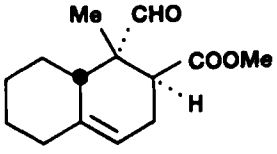
Warren 1983 (198) | Warren 1983 (199) | Warren 1985 (200) | Warren 1985 (201)



Warren 1984
(202)



Warren 1985
(203)



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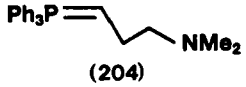

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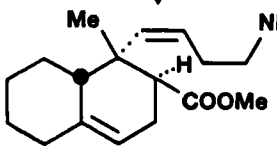
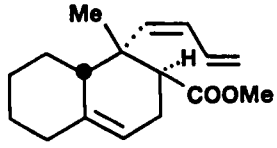
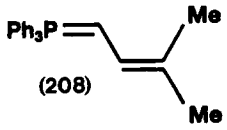


(206)

(1), (2)



Corey *et al* 1985
(207)



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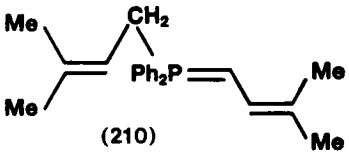
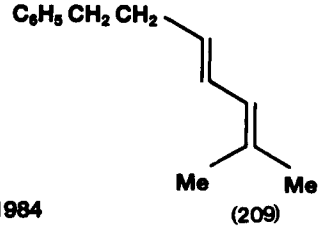


(210)

(3)



(209)

Vedejs, Fang 1984

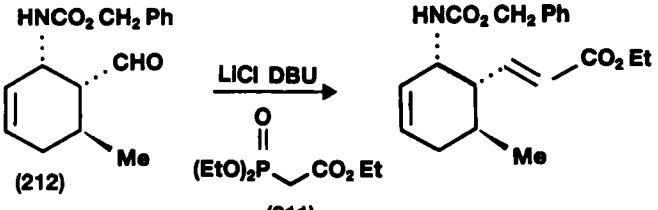
E:Z
1.2:1
>15–4.8:1

(1) m-Cl C_6H_4 CO_3H, 0°C
(2) 50°C
(3) $PhCH_2$ CH_2 CHO

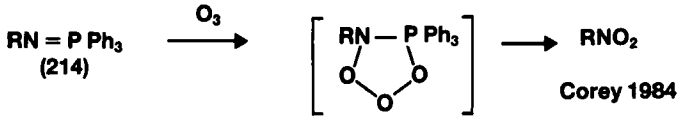
triphenylphosphorane, reacted, with difficulty, only on the γ-carbon with hindered aldehyde (205). Vedejs, 1984 has also been able to devise[188] an improved 1,3-diene synthesis based upon the Wittig reaction, this time with E-selectivity. Moderated Wittig reagents generally give impractical E,Z mixtures of 1,3- dienes as in the synthesis of (209) with ylide (208)-butyllithium. Vedejs replaces one of the phenyl substituents by allyl as in ylide (210) and observes a dramatic increase in E-olefin production, the effect being greater for sodium and potassium bases than with lithium.

The above examples illustrate the exciting variations that recently have been made with the basic Wittig reaction to improve selectivity to Z- or E-olefins at will. It is anticipated that further examples in this area will be reported in the future. The Horner/Wadsworth-Emmons modification of the Wittig reaction has been used to great effect for E-selective olefin synthesis. This procedure requires strong bases to deprotonate phosphonate such as (211) and this can cause problems when reaction with base-labile aldehydes such as (212) is desired. Masamune and Roush, 1984 have now found[189] that in the presence of lithium ions, (211) may be deprotonated with an amine such as DBU. Such mildly basic conditions have allowed the production of E-olefin (213) in 85% yield without epimerisation. Rathke, 1985 at the same time observed[190] that in the presence of magnesium or lithium halides, the less expensive base triethylamine may be used in a similar manner.

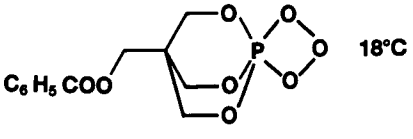
Corey, 1984 has developed a new synthesis of organic nitro-compounds based on the ozonolysis of Staudinger phosphine imines (214). This procedure is effective for the conversion of hindered halides which do not undergo displacement with silver nitrite. Phosphite ozonides are useful reagents for generating singlet oxygen which is a valuable oxidising agent. Keehn, 1985 has continued his search for such a reagent which is stable at 25°C and reports[192] the most stable phosphite ozonide to date (215) with a half-life of >100 minutes at 18°C. Stabilisation by the remote



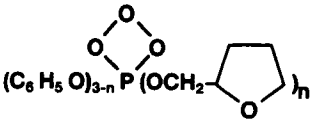
Masamune, Roush 1984
(213)



Corey 1984

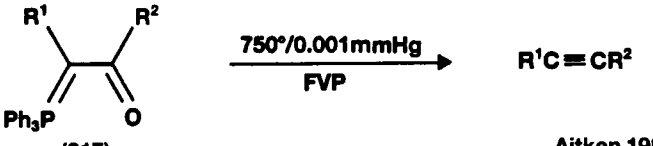


Keehn 1985
(215)

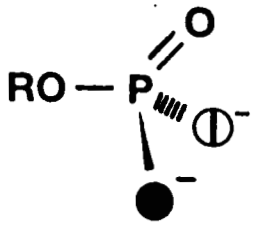


Koenig 1985
(216)

n = 1 −34°C
n = 2 −70°C
n = 3 −85°C



Aitken 1985



" On the back of a postage stamp "

substituent is postulated. Koenig, 1985 has prepared[193] the novel phosphite ozonides (216) which are clean and efficient singlet oxygen generators at low temperature.

Finally, Aitken, 1985 has converted[194] β-oxoalkylidene-phosphoranes (217) into alkynes by flash vacuum pyrolysis. Products were obtained pure and in high yields. This is a particularly important synthetic procedure, as conventional pyrolysis with (217) where R^1 and R^2 are both H or alkyl groups fails.

CONCLUDING REMARKS

If I were required to write on the back of a postage stamp, and provided it was one of those issued in the U.K. for 29th July 1981 or 23rd July 1986, the most important advances made in organophosphorus chemistry over the last decade, I would draw three structures.

These for me encompass the excitement that has been generated and the discoveries that have been made so recently in our field and these three structures have formed the focus of this presentation today.

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