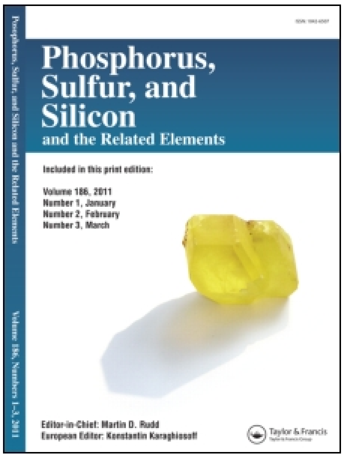

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THE THERMOLYSIS OF PENTA-COORDINATE PHOSPHORUS HETEROCYCLES

James B. Husband[a]; Hamish McNab[a]
[a] Department of Chemistry, University of Edinburgh, Edinburgh, UK

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THE THERMOLYSIS OF PENTA-COORDINATE PHOSPHORUS HETEROCYCLES

JAMES B. HUSBAND and HAMISH McNAB*

Department of Chemistry, University of Edinburgh, West Mains Road,
Edinburgh EH9 3JJ, UK

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1. INTRODUCTION

Small-ring heterocycles are an important class of penta-coordinate phosphorus compounds, whose properties—including thermolysis—have been extensively studied.[1,2] It is noteworthy that these compounds display a wide range of thermal stability—certain examples decompose completely below −40°C, while others are stable indefinitely at > 300°C—yet any thermolysis reaction almost invariably takes place at the phosphorus centre. Diverse conditions have been employed: reactions have been carried out in the melt, in solution and in the gas phase, and ionic, radical and concerted mechanisms have been advanced to explain the results. In this article, we hope to rationalise this behaviour and to give a representative survey of the field. Unfortunately, a truly comprehensive review is literally not possible at this time, since in the older literature, P(v) intermediates are often written without evidence of their existence, or, betaine structures are assigned to species which are in fact phosphoranes. Two classic reactions of organophosphorus chemistry, the Michaelis–Arbusov reaction[3] and the Wittig reaction[4] come into the latter category. Indeed it has been claimed that "historical tradition is the primary remaining basis for the widespread assumption that betaines are key intermediates in the Wittig reaction."[5] We have therefore emphasised examples in which the penta-coordinate species has been isolated or has been clearly characterised *in situ*, (usually by ^{31}P n.m.r. spectroscopy).

Although a few ligand rearrangements are known, the thermolyses are normally characterised by a change of phosphorus coordination number from 5 to 3 or 4: this may be achieved with or without cleavage of the heterocyclic ring (Scheme 1). Although tetra-coordinate phosphorus products are more common, and usually derive from the high stability of the P=O bond, only the formation of P(III) products has attracted general theoretical interest. Early predictions, based on the PH_5 molecule, that such cleavage either involves two equatorial or two axial ligands[6] are supported by most recent calculations,[7] though the potential energy surface is very sensitive to the level of basis set, even for such "simple" model systems. Apparently, no experiments have been explicitly designed to test these predictions.

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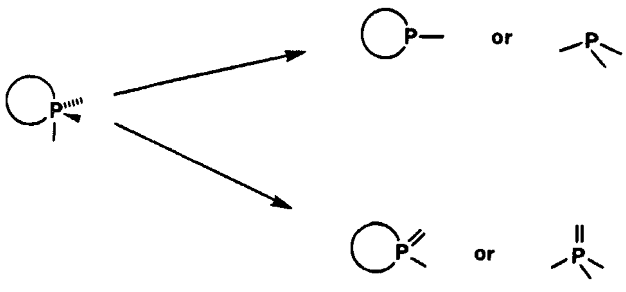
*Author to whom all correspondence should be addressed. No reprints available.

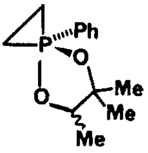


SCHEME 1

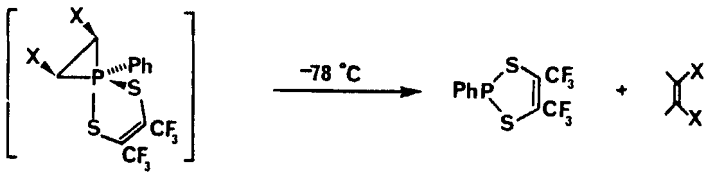
In the examples which follow, the P(v) compounds are grouped according to the smallest P-containing ring, and sub-grouped according to heteroatoms and oxidation level of the ring.

2. THREE-MEMBERED RINGS

Denney has shown that ethylene is obtained from the strained phosph(v)iran derivatives (**1**)[8] and (**2**)[9] at low temperatures. The dithia-derivative (**2**; X = H) is too unstable for detection, even at −78°C, but, in an important experiment, its decomposition was shown to be at least 95% stereospecific (Scheme 2, X = ^{2}H) as predicted for a concerted mechanism[9] (c.f., Section 4.1).



(**1**)



(**2**)

SCHEME 2

3. FOUR-MEMBERED RINGS

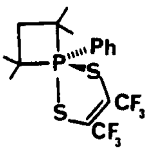
3.1. *Phosph(v)etans*

Such phosphoranes are rare, but are much more stable than corresponding three-membered rings. Thus, decomposition of (**3**) gave the intact phosphetan sulphide "at elevated temperatures",[10] while (**4**) shows standard reactions of the dioxaphospholan moeity[11] (Section 4.3).

3.2. Oxaphosph(v)etans

This ring system (**5**) is arguably the most important of all P(v) systems for synthetic chemists, since it is either a transition state or an intermediate in the Wittig reaction[4] (Scheme 3). In the absence of complications due to lithium halides,[4] low temperature ^{31}P n.m.r. methods show conclusively that oxaphosph(v)etans are indeed the only observable *intermediates* in these reactions.[5,12] There is still theoretical[13] and experimental[5,12] speculation as to the precise mode of formation and decomposition of (**5**), especially with regard to the influence of substituents on stereochemistry.

Certain unusually stable, isolable phosph(v)etans have been known for nearly twenty years,[14] though their thermolysis at temperatures of up to 100°C generally produces the expected "Wittig" product. (See also Section 4.3.) Stabilising features include an exocyclic double bond e.g., (**6**)[15,16] or incorporation into a spiro system, e.g., (**7**).[17]



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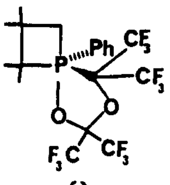

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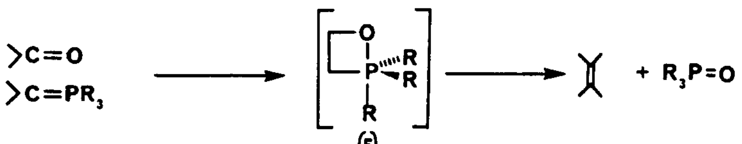
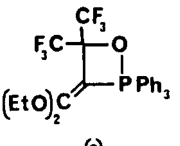


(5)

SCHEME 3



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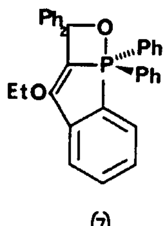


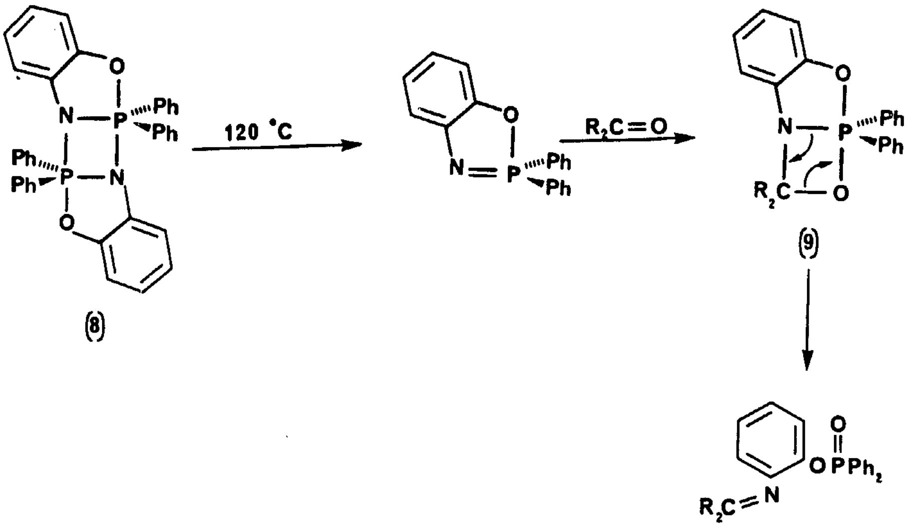
(7)

3.3. Oxazaphosph(v)etans and Diazadiphosph(v)etidines

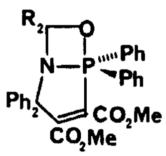
Diazadiphosph(v)etidines[18] e.g., (**8**) are formal dimers of phosphinimines, and the reverse of this dimerisation process is the most common thermolysis route. The phosphinimine may itself be stable,[19] or isomerise,[20] or it can be trapped with carbonyl compounds[21,22] (e.g., Scheme 4). Isolated examples of highly stable diazadiphosph(v)etidines have been reported.[23] Certain highly reactive phosphinimines combine with carbonyl compounds under such mild conditions that the intermediate oxazaphosph(v)etan corresponding to (**9**) can actually be isolated, e.g., (**10**; R ≠ H).[24-26] Further heating completes the sequence in an analogous manner to Scheme 4. In the particular case of the diphenylketene adduct, the ultimate product is tetraphenylsuccinonitrile, formed by further cleavage of the ring-opened ketenimine and radical dimerisation of the resulting iminyl.[27] Retro-cleavage of oxazaphosph(v)etans to regenerate the phosphinimine is also known:[28] this behaviour is particularly important for the related adducts e.g., (**11**) with isocyanates, for which Wittig-type decomposition is not possible.[29,30]

3.4. Trioxaphosph(v)etans

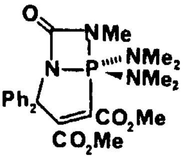
The adducts of ozone and triarylphosphines e.g., (**12**) are now well characterised as P(v) derivatives. They decompose under mild conditions (– 35°C or below)[31] to give singlet oxygen.[32]



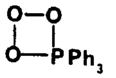
SCHEME 4



(**10**)



(**11**)



(**12**)

4. FIVE-MEMBERED RINGS

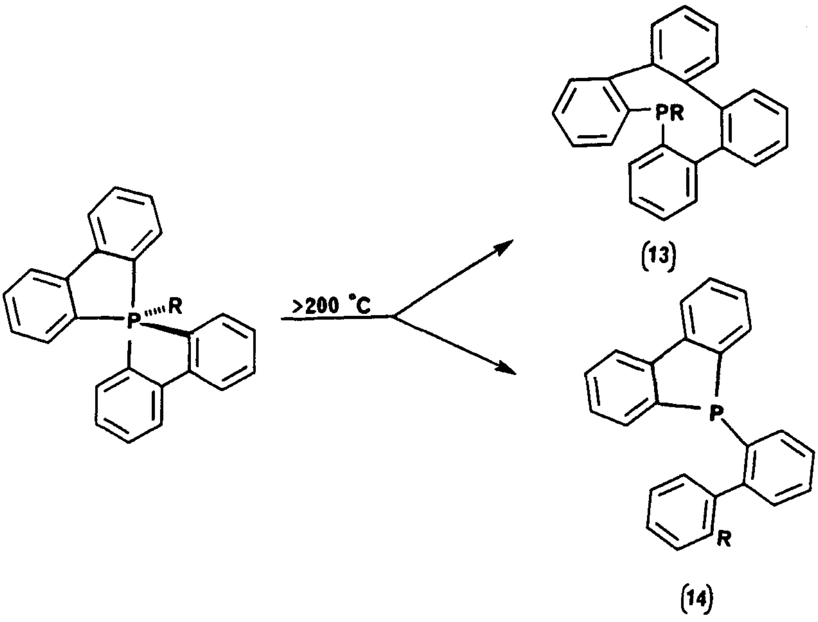
4.1. Phosph(v)oles

For these compounds, the electronegative driving force for the formation of $R_3P{=}X$ is absent, and the reactions are dominated by cleavage or rearrangement to tri-coordinate phosphorus compounds.

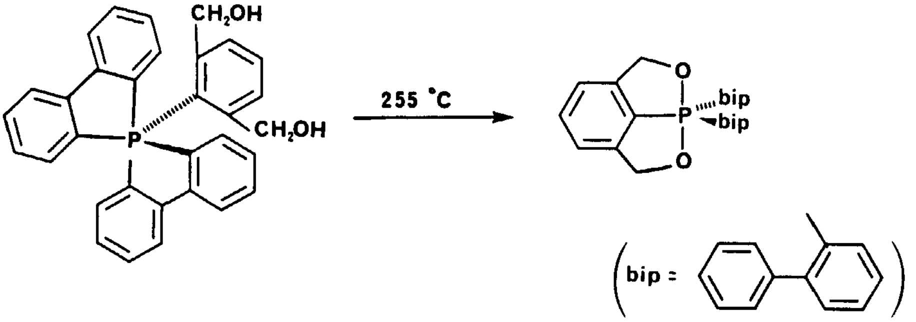
Heavily substituted phosph(v)oles show unusual rearrangements at their melting points to P(III) compounds, by ring expansion or ligand migration[33,34] (Scheme 5). The ratio between the two pathways is influenced—at least in part[33]—by steric factors:[35] the phosphonine (**13**) is favoured by small groups R, while large groups migrate to give the phosphole (**14**). Hellwinkel treats these examples as synchronous cheleotropic reactions, with (**13**) and (**14**) formed by axial–axial and equatorial–equatorial cleavage, respectively. However, for the special case where R = H, there is considerable evidence that free radical intermediates are involved in the formation of (**14**). The reaction is initiated by spontaneous homolysis of the P—H bond to give an observable phosphoranyl radical: hydrogenated products and a radical dimer are also obtained as minor products.[36]

In a related reaction, reactive *o*-groups on R can cause isomerisation of the phosphorane[37] (Scheme 6).

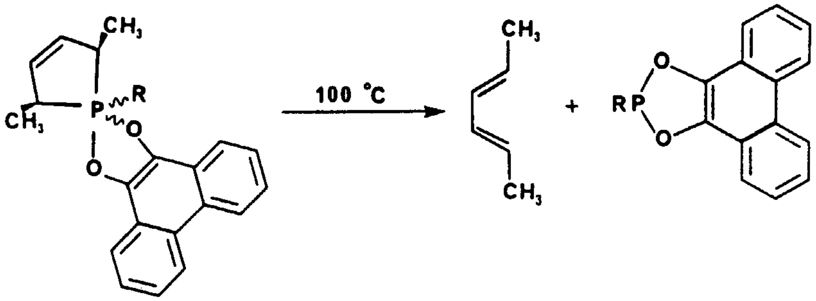
2,5-Dihydrophosph(v)oles fragment stereospecifically to give dienes and P(III) compounds by the predicted disrotatory retrocheleotropic process.[38,39] The mechanism has been best studied by Hall for the isolable spirophosphoranes (**15**) (Scheme 7). Steric effects are again important and control the decomposition rate: the crowded phenyl derivative (**15a**) in which the substituent R is *cis* to the methyl groups is some 10^5 times more labile than the thermally stable *trans*-compound



SCHEME 5



SCHEME 6



(15)

a R = cis - Ph
b R = trans - CH_3

SCHEME 7

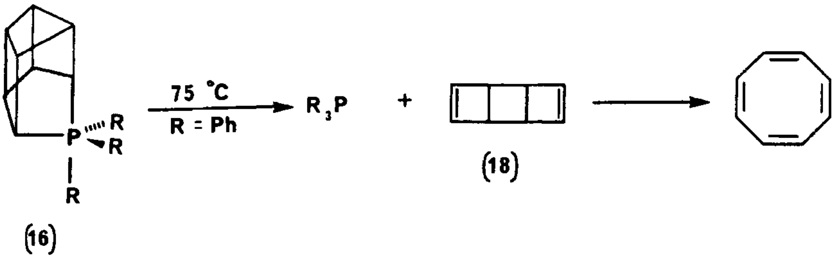
(**15b**). In many related examples the facility of this process renders the products too unstable to isolate.[38,40,40a] Conversely 2,5-dihydrophosph(v)oles without crowding substituents in the 2,5-positions can decompose by alternative pathways, including ligand fragmentation,[41] rather than by the retrocheleotropic process.[42,43]

Dienes are also formed from 2,3-dihydrophosph(v)oles, by prototropic shift to the 2,5-dihydro isomer, prior to fragmentation.[44]

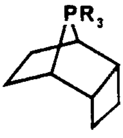
Katz has made a detailed study of intriguing bridged phosph(v)oles e.g., (**16**)[45,46] and (**17**).[47] In all cases except (**17**; R = Me), the P(III) derivative is obtained by six electron-retrocheleotropic fragmentation (e.g., Scheme 8). Once again, steric factors control this process,[48] which becomes easier with increased *P*-aryl substitution. In such favourable cases, the decomposition temperature is sufficiently low that the thermally unstable diene intermediate (**18**) may be isolated.

Similar reactions have been observed for the bridged phosphole (**19**) which gives cyclooctatetraene on thermolysis in methanol.[49] A penta-coordinate intermediate is implicated.

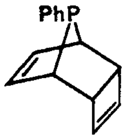
The phosph(v)olan (**20**) shows n.m.r. evidence for loss of methanol at temperatures above 40°C to form an ylide.[50]



SCHEME 8



(17)



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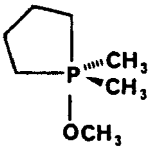


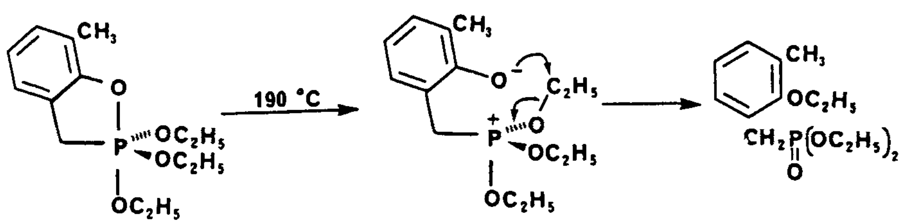
(20)

4.2. Oxaphosph(v)oles

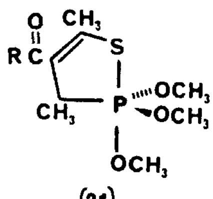
In most derivatives of this ring system which have been studied the heteroatoms are situated in adjacent positions; the formation of tetra-coordinate phosphorus oxides is therefore the dominant reaction, although there are cases in which P(III) extrusion is observed.

Benzoxaphosph(v)olenes can give tetra-coordinate phosphorus products by an intramolecular ligand reorganisation formally related to the Arbusov reaction (Scheme 9),[51] a reaction which is observed under much milder conditions for the thia-analogue (**21**).[52] For the special case of the *P*-hydroxy compound (**22**), the tetra-coordinate tautomer is in true equilibrium with the phosphorane.[53] Bicyclic oxaphosph(v)olenes show expected thermal stability: the fluorenyl derivative (**23**) is an interesting example,[54,55] since it is *formed* at 200°C by dehydration of a phosphorus oxide—the reverse of usual behaviour—despite the fact that the product has an "unstable" equatorial–equatorial configuration for the fluorenyl five-membered ring. Unfortunately since this ligand arrangement might have provided a test of theoretical predictions,[6] no well defined thermolysis behaviour could be observed at higher temperature.

Bicyclic oxaphosph(v)olones can also be thermally stable: some examples are unchanged after at least 30 min at 340°C.[56,57] A different arrangement of the bicycle allows internal nucleophilic attack of the betaine[58] (Scheme 10— c.f., Scheme 9),



SCHEME 9



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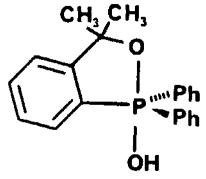

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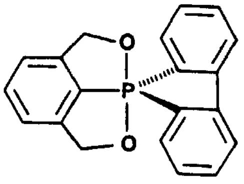

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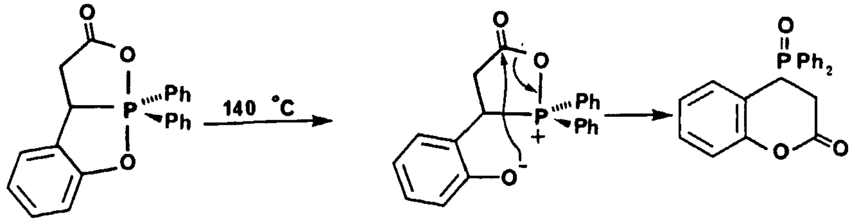
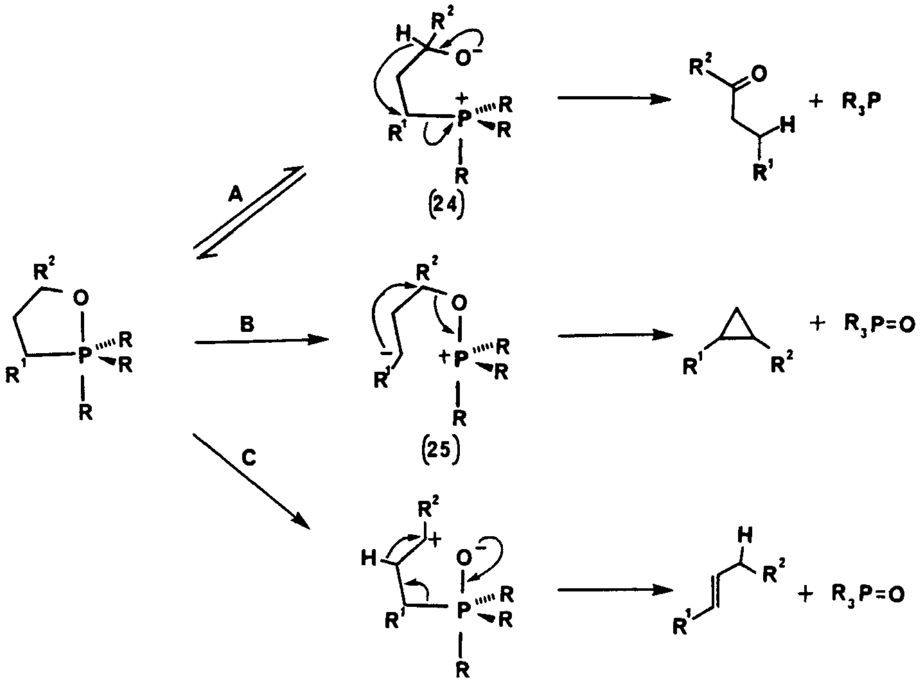


SCHEME 10

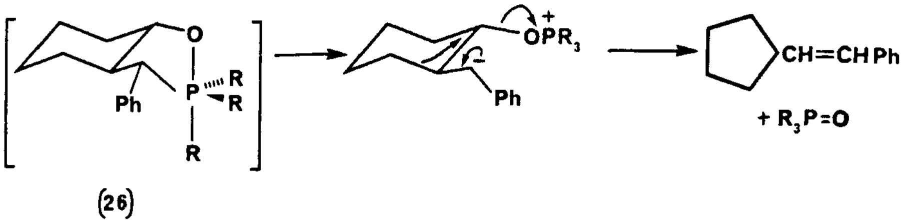
while in other similar cases, *inter* molecular attack allows the formation of useful polymers.[59]

The chemistry of the fully reduced oxaphosph(v)olan system is particularly complex, since ketones, alkenes, cyclopropanes, and other products can be formed at high temperatures, depending on substituents and reaction conditions. These phosphoranes are generally prepared by reaction of an ylide with an epoxide, and only in certain cases is their intermediacy well established. The thermolysis situation was rationalised by Trippett[60] in 1963 (Scheme 11). Under normal circumstances, P—O heterolysis takes place to give the betaine (**24**) which can collapse with a hydrogen shift and loss of the P(III) species to generate a ketone[61,62,63] (route A). However, if R^1 can stabilise a carbanion, then cyclopropane formation is dominant, presumably by rear-side attack of the betaine (**25**): optical activity of an epoxide precursor is indeed found in the product[64] (route B). Yields of cyclopropanes (R^1 = CO_2Et) of 30–60% can be obtained. C—O heterolysis, followed by migration may explain the formation of alkenes,[61,62] (route C) though it seems unlikely that the specific C—C migration observed from the cyclohexyl compound (**26**)[65] could involve the planar carbocation required by this route. A concerted mechanism, or an extension of route B (Scheme 12) is perhaps more likely in this case.

Extensions of these reactions over the last twenty years have produced further variations of route A (Scheme 11). Hydrogen abstraction from alkyl groups in position 3 (R^1) leads to unsaturated alcohols,[63] while under extreme conditions, *P*-phenyl migration[66] is even possible, for which "internal collapse" appears to be the accepted explanation[67] (Scheme 13). Under milder conditions, the betaine (**24**) can tautomerise to the ylid (**27**) which can be trapped in normal fashion by aldehydes or ketones to give E:Z alkenes in a 1:1 ratio.[68] The phosphorane therefore acts as a synthon for γ, δ unsaturated alcohols, and, since the original



SCHEME 11



SCHEME 12

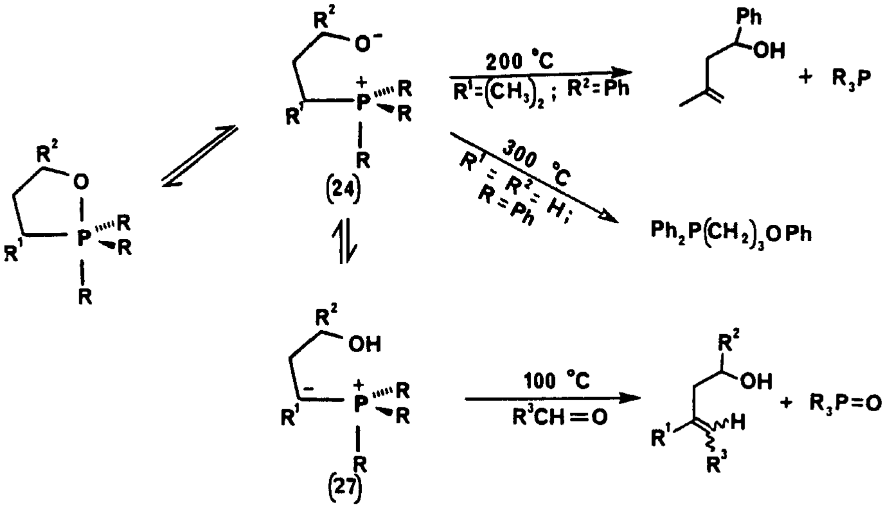
report, it has been used to make exo-methylene cyclic alcohols,[69] and key intermediates in terpene synthesis.[70] The formation of 2,5-dihydrofurans from α-hydroxyketones and vinyltriphenylphosphonium bromide,[71] from which a 2-oxaphosph(v)olan has been isolated[72] may take place by a similar process.

In one example of a 1,3-oxaphosph(v)olan, P(III) extrusion from (**28**) under mild conditions gives ketene dimer, possibly by an ionic mechanism.[73]

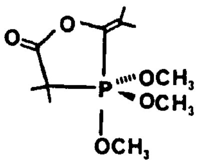
4.3. *Dioxaphosph(v)oles*

The thermolysis of 1,3,2-dioxaphosph(v)oles has been widely studied at both possible oxidation levels of the heterocycle.

An early report[74] that the phospholene (**29**; R = Bu) dissociates to the phosphite on attempted distillation may be explicable in terms of a retrocheleotropic mechanism, though it should be noted that the formation of such phosphoranes from P(III) compounds and α-dicarbonyl derivatives apparently involves ion radical inter-



SCHEME 13



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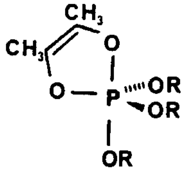

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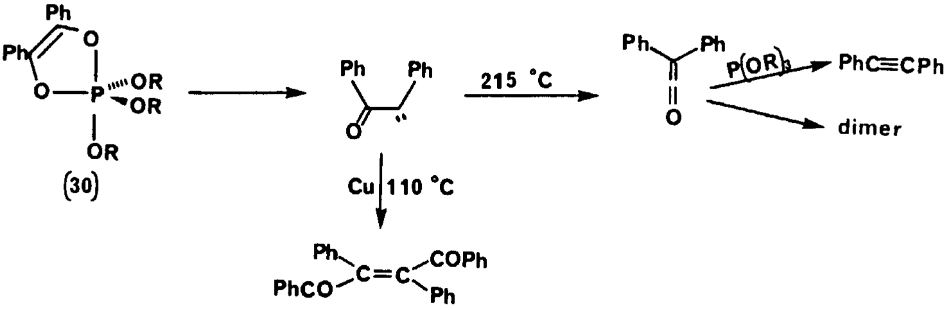
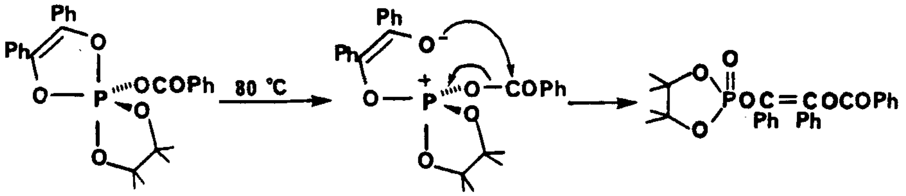


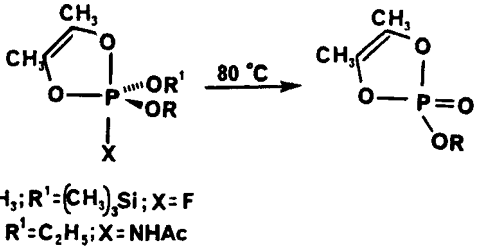
SCHEME 14

mediates.[75] In any event, the thermolysis process is extremely sensitive to structural features: the triethoxy derivative (**29**; R = Et) gives triethyl phosphate (61%),[74] and the trimethoxy analogue (**29**; R = Me) gives equimolar quantities of phosphate and phosphite, together with biacetyl,[76] while only trimethyl phosphate is obtained from the diphenyl derivative (**30**; R = Me).[76] One complication is possible oxidation of the phosphite by the α-diketone co-product: a systematic study of these reactions by flow pyrolysis methods[77] would at least resolve this difficulty.

In the presence of excess phosphite,[78] thermolysis of (**30**; R = Et) gives triethyl phosphate (88%) together with diphenylacetylene (60%) which is probably formed by



SCHEME 15

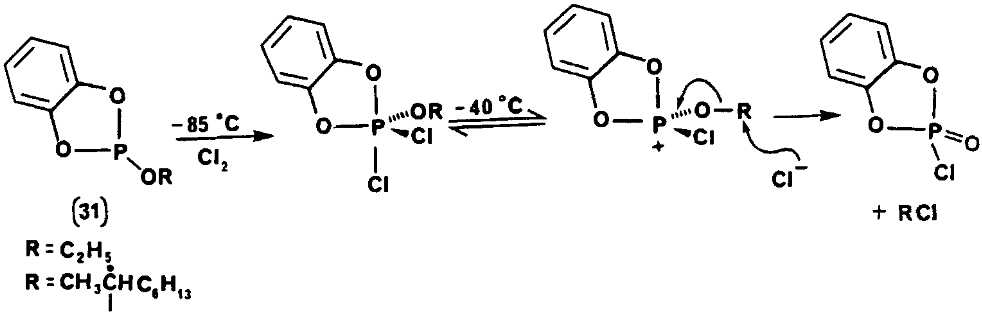


SCHEME 16

deoxygenation of an intermediate diphenylketene.[79] The ketene dimer was also isolated in 24% yield. These results suggest that phosphate extrusion from (**30**) can lead to a carbene, which gives the ketene by Wolff rearrangement (Scheme 14). Suppression of this rearrangement at lower temperatures and in the presence of a copper catalyst[80] leads instead to dibenzoylstilbene.[81]

The presence of labile groups on phosphorus can promote thermal rearrangement reactions[82,83] (e.g., Scheme 15), also found for dithiaphosph(v)olenes.[84] Alternatively, cleavage reactions can leave the phosph(v)olene ring intact[85,86] (e.g., Scheme 16). This behaviour has been closely studied in the benzannelated series,[87] in connection with the mechanism of the Michaelis–Arbusov reaction.[3] For example, treatment of the phosphite (**31**; R = Et) with elemental chlorine at low temperatures gives an observable penta-coordinate intermediate, which leads to the Arbusov product at −40°C[88] (Scheme 17). The classical dissociative mechanism[89] was established by the isolation of an inverted halide when the optically active phosphite (**31**; R = $\mathrm{CH_3\overset{|}{\underset{*}{C}}HC_6H_{13}}$) was used[90] (Scheme 17).

At the fully reduced oxidation level, 1,3,2-dioxaphosph(v)olans typically extrude



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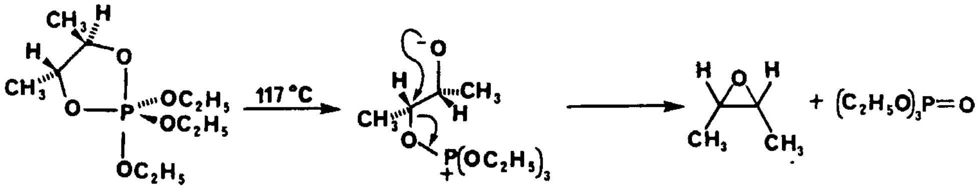


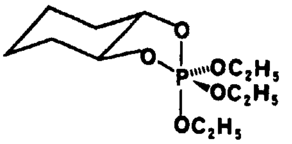
SCHEME 18

tetra-coordinate phosphorus species to give epoxides. The reaction has been applied to a large number of cases: substituents at C(4) and C(5) include alkyl,[91] aryl[92] and cyano[93-95] groups, while phosphorus ligands include alkoxy,[91] dialkylamino[92,96] or phenyl[97] groups. In favourable cases, preparative yields of over 90% are obtained.[98] A wide range of conditions has been employed,[92] which often depends on the substituents, but a few hours at temperatures of 80–90°C appears to be typical.

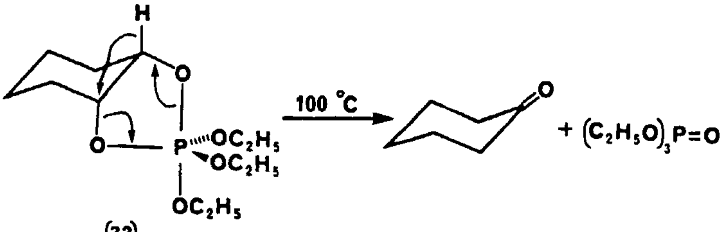
The reaction is stereospecific, with *trans*-4,5-disubstituted dioxaphosph(v)oles generating the *cis*-epoxide.[91,92,98] This result establishes a heterolytic cleavage mechanism, followed by intramolecular rear-side attack of the betaine (Scheme 18), but casts doubts on the mode of isomerisation of *cis*-stilbene oxide in the presence of tributylphosphine oxide under drastic conditions.[99] However, the method has been successfully applied to a three step *stereospecific* synthesis of *cis*-stilbene oxide from *trans*-stilbene[100] and has been used to assign the stereochemistry of a dioxetane.[101] Sometimes the betaine is formed without apparent involvement of the phosphorane, and can lead to the epoxide directly.[96]

In one interesting demonstration of stereospecificity, the *trans*-cyclohexyl derivative (**32**) unexceptionally gives cyclohexene oxide, at room temperature, while the *cis*-isomer (**33**), for which such antiperiplanar attack is impossible, gives cyclohexanone, by hydrogen migration at much higher temperatures (100°C)[102] (see below, and Scheme 19).

A careful kinetic study of the formation (by the peroxide method) and subsequent decomposition (Scheme 20) of the triaryl derivatives (**34**) shows good correlation of thermolysis rate with the Hammett σ-parameter of the *P*-aryl groups ($\rho =$

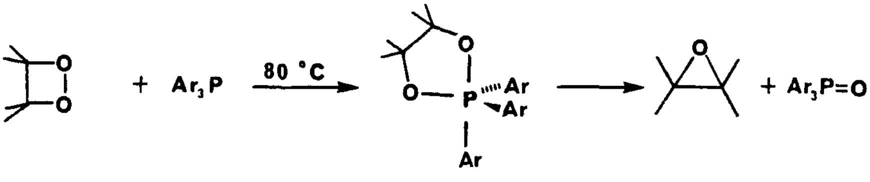


(**32**)



(**33**)

SCHEME 19



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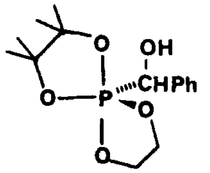
SCHEME 20



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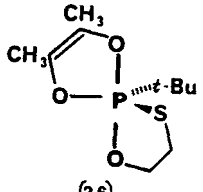


(36)

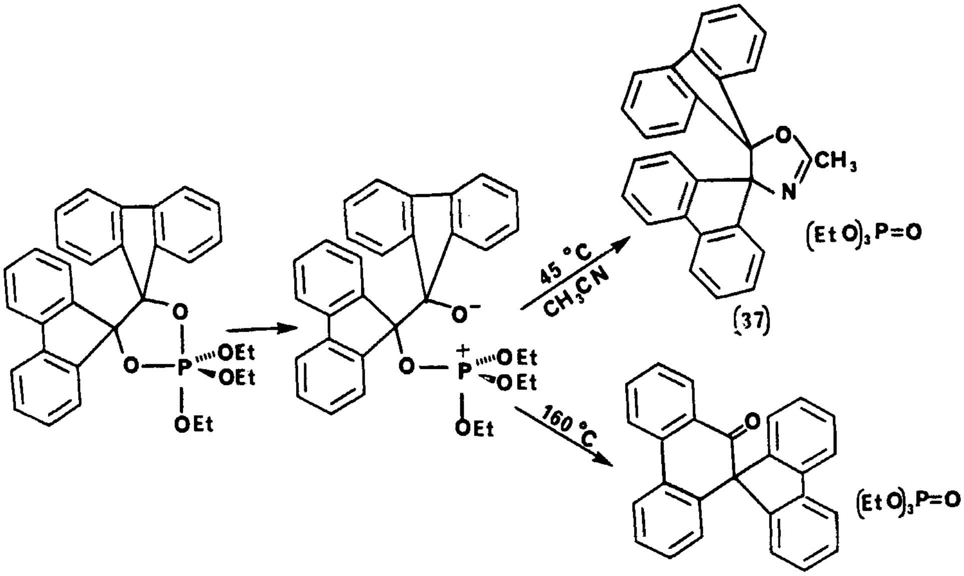
-3.51).[103,104] This is consistent with positive charge development on phosphorus in the slow step, which is therefore identified as the initial cleavage to give the betaine (Scheme 18).

In two cases where competitive formation of epoxides is possible, ethylene oxide rather than its tetramethyl derivative is obtained from (**35**),[105] though ethylene sulphide, rather than ethylene oxide, is obtained from (**36**).[106]

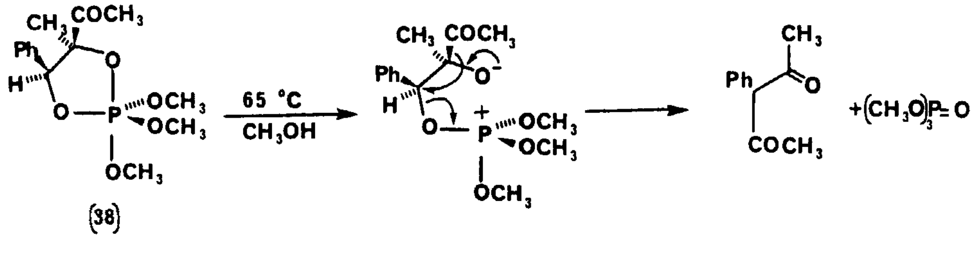
In a number of instances, thermolysis of 1,3,2-dioxaphosph(v)olans leads to migration (c.f., Scheme 19) or ring contraction products, rather than to epoxides. Where a highly crowded epoxide would result, a pinacol-type rearrangement can take place to give ketones[107,108] (e.g., Scheme 21). The proposed betaine intermediate has been trapped to give the oxazoline (**37**; 71%).[108] The thermolysis conditions are dependent on the phosphorus ligands,[107] and fluorenone is often formed by a competitive process.[109] These results rationalise the findings of earlier experiments on the fluorenone systems,[110] and also the formation of desoxybenzoin from benzoin and phosphite,[111,112] though in the latter cases, the possibility of an intermediate epoxide was apparently not rigorously excluded.

Similar migrations, but of acyl groups, are observed when certain acyldioxaphosph(v)olans are heated in methanol[113] (Scheme 22). Epoxides are not intermediates in these reactions.[113] Although the solvent plays no obvious part in the mechanism, the reactions are clearly accelerated by conditions of high polarity. Thus, in contrast, (**38**) shows only *cis–trans* isomerisation in boiling xylene.[113] 4,5-Diacyl derivatives show different rearrangements in methanol to give enol lactones which may react further with the solvent[113-115] (Scheme 23).

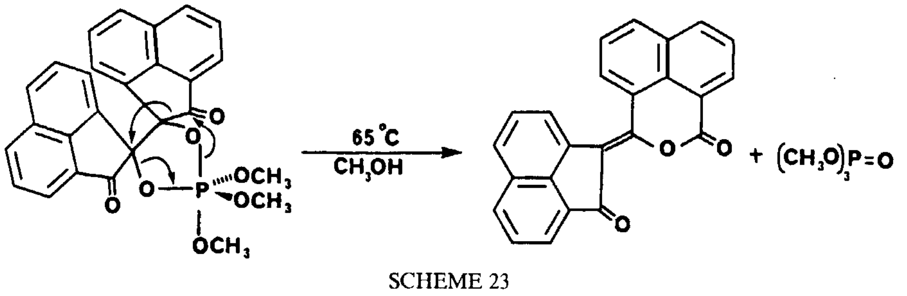
In one case, migration to the positive phosphorus centre of the betaine intermediate gives an unusual phosphorane rearrangement[116] (Scheme 24). An even more remarkable rearrangement takes place with 4,5-tetra(trifluoromethyl)dioxaphosph(v)olans and related compounds, in which ring contraction gives stable oxaphosph(v)etans (Scheme 25).[117,118,11] The rearrangement is general for a range of alkyl and aryl ligands, with the thermolysis of the triethyl compound being the most facile. The mechanism is thought to involve cleavage of hexafluoroacetone, tautomerism of the



SCHEME 21



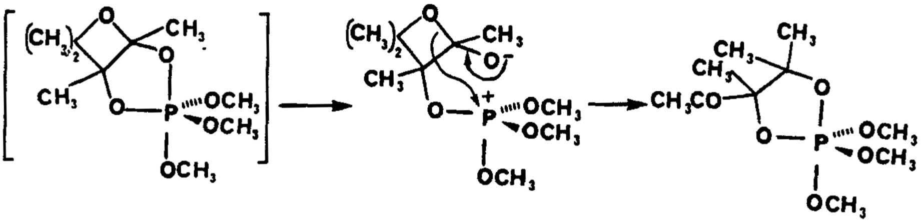
SCHEME 22



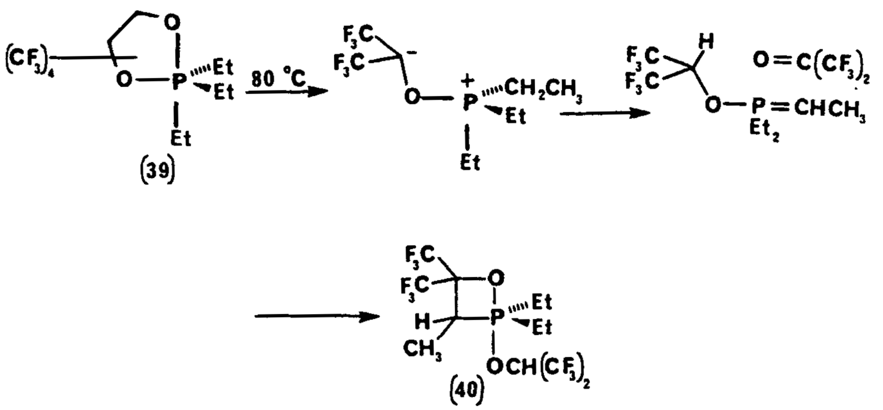
SCHEME 23

betaine to an ylide, and subsequent recombination: the ketone is indeed detectable in closely related reactions (see below). Further thermolysis of the adducts (**40**) give alkenes by standard mechanism.[11,117]

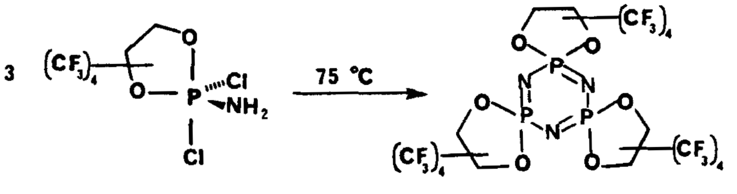
Some trivial tautomerisations of P—H[119] and P—OH[120,121] phosphoranes to give tri-coordinate and tetra-coordinate species and a related isomerisation of an anion[122] have been reported. Examples of ligand fragmentation include Me_3SiF elimination



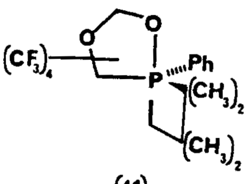
SCHEME 24



SCHEME 25



SCHEME 26



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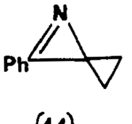


(44)

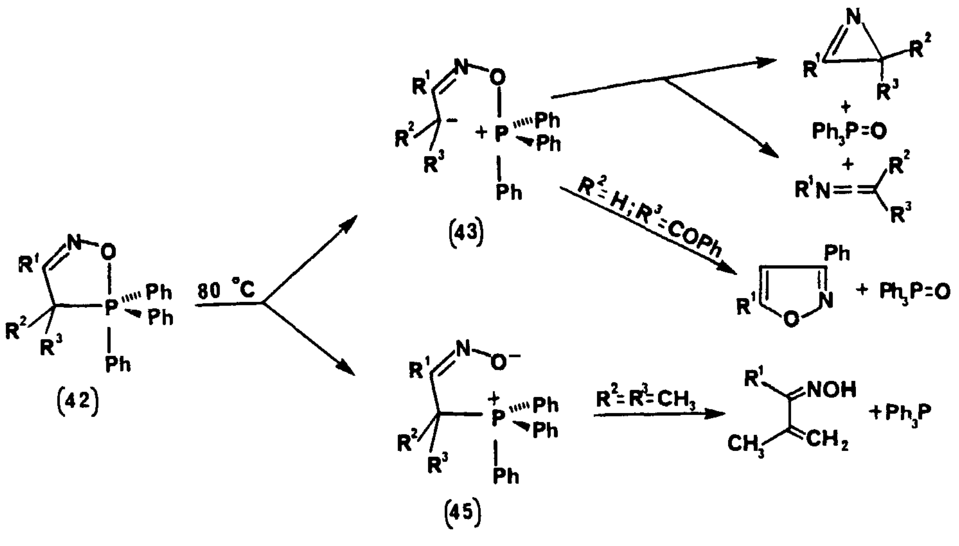
(c.f., ref. 85) to give diazadiphosphetidines,[123,124] and one unusual case in which *double* elimination gives a cyclic phosphazene[125] (Scheme 26).

The few studies of 1,4,2-dioxaphosph(v)olans are intimately connected with the ring contraction (Scheme 25) described in a previous paragraph. Thus the initial reaction of hexafluoroacetone or pentafluorobenzaldehyde with a P(III) reagent may[126] give a 1,4,2-dioxaphosph(v)olan e.g., (**41**) as a kinetically stable product,[127,128] which can—but not always[129]—rearrange to the 1,3,2-isomer.[11] In one case the complete rearrangement from a 1,4,2-dioxaphosph(v)olan to an oxaphosph(v)etan takes place directly, with no other P(v) derivative observable by n.m.r. spectroscopy.[130] 1,4,2-Dioxaphosph(v)olans have also, with rather less evidence, been suggested as intermediates in the formation of epoxides from hexamethylphosphorous triamide and carbonyl compounds.[131,132]

4.4. Oxazaphosph(v)oles

A number of isomeric oxazaphosph(v)oles are known in a range of oxidation levels. Since all the examples have adjacent phosphorus and oxygen atoms, the formation of tetra-coordinate phosphorus products represents the major thermolysis pathway, though a variety of mechanisms is involved.

The behaviour of the 1,2,5-oxazaphosph(v)olene system (**42**) is particularly complex and can give azirines, ketenimines, or other products.[133,134] However, Bestmann has provided a rationale[134] (Scheme 27) similar in scope to that of Trippett for 1,2-oxaphosph(v)olans (Schemes 11 and 12). Thus electron-withdrawing groups R^2, R^3 promote P—C heterolysis to give (**43**): such phosphoranes are particularly unstable and may not be isolable. Electron delocalisation of the carbanion centre reduces its nucleophilicity, and so rearrangement to the ketenimine, rather than azirine formation takes place (e.g., R^1 = Ph, R^2 = Me, R^3 = CO_2Et). The stability of the phosphorane is increased by electron donating groups R^2, R^3 and the increase in nucleophilicity diverts the intermediate (**43**) to the azirine (e.g., R^1 = Ph, $R^2 = R^3$ = Me), though both routes may compete.[135,136] In favourable cases, azirines[137,138]—some of exotic structure[139] e.g., (**44**)[134,140]—are conveniently made in this way, and their properties have been studied.[141-143] The presence of a ketone group at the 4-position allows another mode of decomposition from the betaine (**43**) to give excellent yields of isoxazoles[144,145] (Scheme 27). P—O heterolysis of (**42**) to (**45**) requires *both* an electron-withdrawing group R^1 and an alkyl group R^2, R^3 to



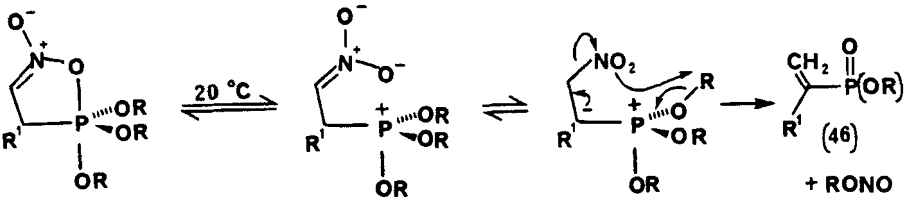
SCHEME 27

generate the unsaturated oxime by hydrogen shift[134] (e.g., $R^1 = CO_2Et$, $R^2 = R^3 =$ Me).

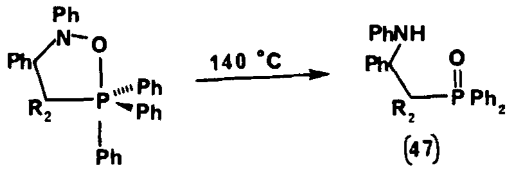
The *N*-oxide derivatives of these oxazaphosph(v)olenes are of interest as possible intermediates in deoxygenation reactions of nitroalkenes to give indoles,[146] but their thermolysis apparently takes alternative, more complex pathways[147–149] (Scheme 28). The formation of the phosphonate (**46**) may be rationalised in terms of ring opening, tautomerism, and unusual cleavage of the resulting *C*-nitro group. Alkyl nitrites, and small amounts of nitro compounds were also detected.[149]

In one remarkable series of experiments at the fully reduced oxidation level, Huisgen and Wulff discovered that benzyne was *formally* eliminated to give phosphorus oxides (**47**) in yields of up to 50%[150,151] (Scheme 29). Unfortunately, no by-products were reported, but it is possible that N—O homolysis is followed by cleavage of a phenyl radical, followed by hydrogen capture (c.f., Scheme 32). These reactions are long overdue for re-investigation.

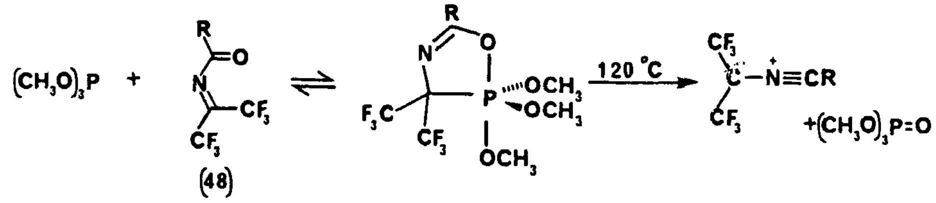
The class of 1,4,2-oxazaphosph(v)oles has been studied exclusively at the phosph(v)olene oxidation level, and almost exclusively by Burger using fluorinated substrates.[2] Pyrolysis for a few hours at 100–140°C causes tetra-coordinate phosphorus extrusion to give nitrile ylids (Scheme 30) as confirmed by competitive trapping experiments.[152] Much of the interest derives from the subsequent chemistry of this 1,3-dipole, which can be trapped by cycloaddition with alkenes and alkynes[152–55] or enol ethers,[156,157] to give 2*H*-pyrroles or pyrrolines, with azo-compounds[158] to give 3*H*-1,2,4-triazines, with nitriles[158] or carbonyl compounds[158] to give 4*H*-imidazoles or oxazolines. The use of pyridine[159,160] or related compounds as dipolarophile allows addition to the C=N bond to generate fused imidazoles, while an unusual [3 + 1] cycloaddition takes place with isocyanides[161,162] to give iminoazetines. Reactions with phenylacetylene[163] and nitrosobenzene[164] are more complex, but lead to well-defined products; intramolecular cycloadditions have also been observed.[165] A further complication is a competitive, and presumably reversible[166] retrocheleotropic process to give the electron-deficient diene (**48**) (Scheme 30) which can be trapped by electron-rich dienophiles.[157] In the absence of trapping agents,



SCHEME 28



SCHEME 29



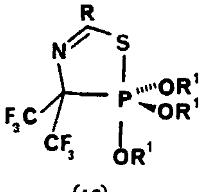
SCHEME 30

dimerisation and cyclisation of the 1,3-dipole can take place.[167] The thio-analogues (**49**) show similar chemistry.[168]

Despite the high efficiencies of these processes—yields are typically 70–80%—a major synthetic limitation is the constraint of bis-trifluoromethyl substitution at position 4. Two examples of other substituents at this site show alternative reactions by intramolecular rearrangement of the 1,3-dipole[169,170] (Scheme 31—c.f., Scheme 27).

In contrast, the thermal chemistry of 1,3,2-benzoxazaphosph(v)olenes is controlled by ligand reactions, so that all three heteroatoms are retained in the major product. Pyrolysis of *N*-alkyl or *N*-aryl derivatives in the gas phase leads to the formation of phosphinates or phosphinamidates, probably by a free-radical cleavage mechanism.[171,172] In agreement with this, bibenzyl was isolated by radical coupling from pyrolysis of (**50**; $R^1 = CH_2Ph$) (Scheme 32).[172] 1,3,2-Benzthiazaphosph(v)olenes show standard Arbusov-type rearrangements.[173,174]

1,3,2-Benzoxazaphosph(v)olenes which are unsubstituted on nitrogen are in equilibrium with a phosphinimine tautomer.[175,176] Incorporation of a potential leaving



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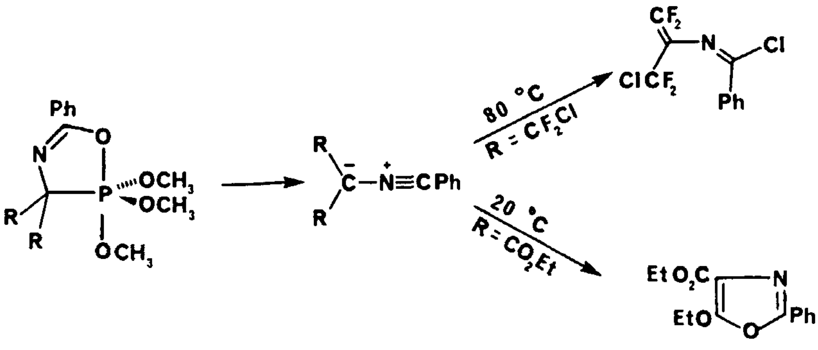
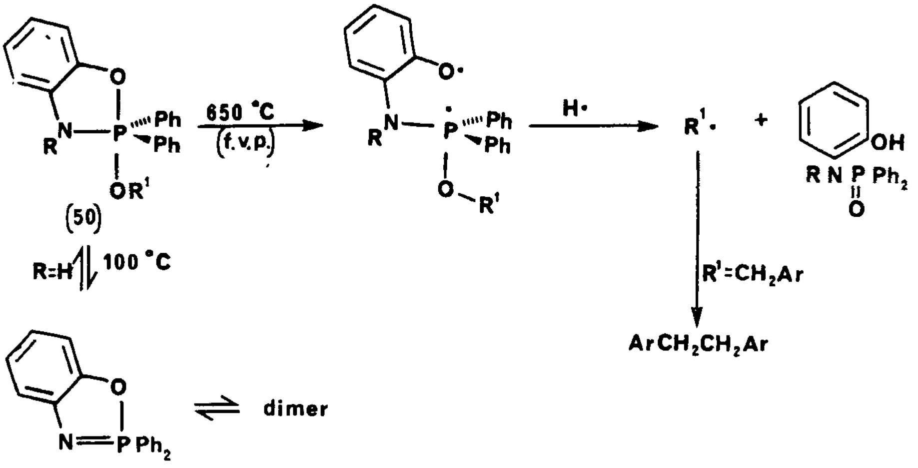


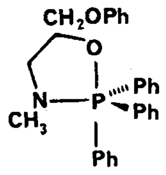
SCHEME 31



SCHEME 32

group at the 2-position allows elimination to give an alternative phosphinimine, which may dimerise, or can be trapped by carbonyl compounds[21,22] (Scheme 32—c.f., Scheme 4). Tautomerisation of certain P—H 1,3,2-oxazaphosph(v)olenes has also been noted.[177]

Aziridines are obtained in high yield from the fully reduced 1,3,2-oxazaphosph(v)olan system e.g., (**51**), at 150° (1 h) though only a few examples are



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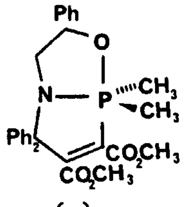

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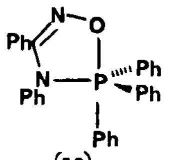

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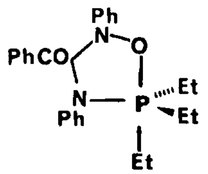

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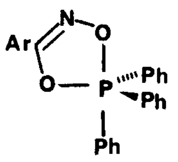

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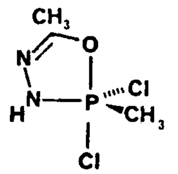

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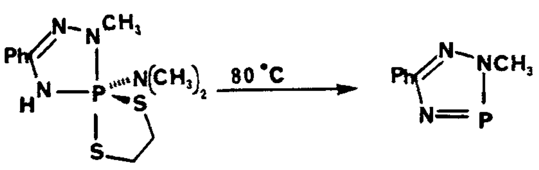


SCHEME 33

known.[178,179] As usual, bicyclic examples are particularly stable, and (52) was recovered unchanged after 5 days at 150°C.[180]

4.5. Phosph(v)oles with Four Heteroatoms

Huisgen and Wulff[181,182] have generated 1,2,4,5-oxadiazaphosph(v)ole systems e.g., (**53**) and (**54**) *in situ* by reaction of phosphinimines with nitrile oxides or with nitrones. Thermolysis under mild conditions gives the appropriate phosphorus oxide, together with a carbodiimide or amidine, depending on the oxidation level of the starting material. This behaviour requires a 1,2-shift of the substituent at position 4 —c.f., Scheme 27. In a similar manner, dioxazaphosph(v)olenes (**55**) give isocyanates in 60–80% yield after 1 h at 40°C.[183]

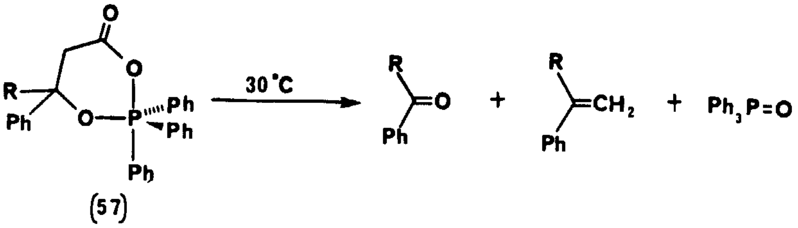
1,3,4,2-Oxadiazaphosph(v)olenes (**56**) also give extrusion of phosphorus oxides on thermolysis *in vacuo* at temperatures of 130°C or less,[184] and there is a suggestion that the liberated nitrile imine may be trapped by dimerisation.[185]

In one unusual report of di- and tri-azaphosph(v)olenes, thermolysis at 80°C causes loss of *three* ligands to generate di-coordinate phosphorus heterocycles[186] (e.g., Scheme 33).

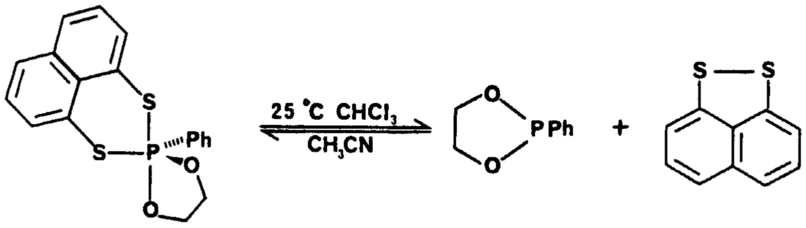
5. SIX-MEMBERED AND LARGER RINGS

In contrast to the situation for four- and particularly five-membered rings, which have attracted a large amount of systematic effort, very little work has been devoted to the thermolysis of large-ring phosph(v)oles, and the limited selection of examples quoted here reflects the rather unsatisfactory nature of this field at present.

For example, Adam gives kinetic evidence for the presence of the phosphorane (**57**) as an intermediate in the insertion of P(III) species into cyclic



SCHEME 34



SCHEME 35

acylperoxides.[187-189] The two major products, whose ratio is dependent on R, are thought to arise by heterolysis of either P—O bond accompanied by CO_2 or ketene formation. Similarly, Denney has proposed seven-membered ring phosphoranes as intermediates in P(III) reactions with cyclic alkylperoxides,[43] or in ligand exchange reactions with diols.[102] Cleavage of the seven-membered ring is suggested by the formation of tetrahydrofuran in competition with other decomposition processes. A dithia-analogue decomposes by a retro-insertion reaction, in a process which is strongly solvent dependent[190] (Scheme 35).

ACKNOWLEDGMENT

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REFERENCES

1. D. Hellwinkel in G. M. Kosolapoff and L. Maier, *Organic Phosphorus Compounds*, Vol. 3, Wiley Interscience, New York (1972).
2. K. Burger in J. I. G. Cadogan, *Organophosphorus Reagents in Organic Synthesis*, Academic Press, London (1979), Chap. 11, p. 467.
3. A. K. Bhattacharya and G. Thyagarajan, *Chem. Rev.*, **81**, 415 (1981).
4. I. Gosney and A. G. Rowley in ref. 2, Chap. 2, p. 17.
5. E. Vedejs, G. P. Meier and K. A. J. Snoble, *J. Am. Chem. Soc.*, **103**, 2823 (1981).
6. R. Hoffman, J. M. Howell and E. L. Muetterties, *J. Am. Chem. Soc.*, **94**, 3047 (1972).
7. W. Kutzelnigg and J. Wasilewski, *J. Am. Chem. Soc.*, **104**, 953 (1982).
8. B. D. Campbell, D. B. Denney, D. Z. Denney and L. S. Shih, *J. Chem. Soc., Chem. Commun.*, 854 (1978).
9. D. B. Denney and L. S. Shih, *J. Am. Chem. Soc.*, **96**, 317 (1974).
10. B. C. Burros, N. J. De'Ath, D. B. Denney, D. Z. Denney and I. J. Kipnis, *J. Am. Chem. Soc.*, **100**, 7300 (1978).
11. R. K. Oram and S. Trippett, *J. Chem. Soc., Perkin Trans. 1*, 1300 (1973).
12. H. J. Bestmann, *Pure Appl. Chem.*, **52**, 771 (1980).
13. R. Höller and H. Lischka, *J. Am. Chem. Soc.*, **102**, 4632 (1980).
14. G. H. Birum and C. N. Matthews, *J. Chem. Soc., Chem. Commun.*, 137 (1967).
15. R. W. Saalfrank, W. Paul and H. Liebenow, *Angew. Chem.*, **92**, 740 (1980); *Angew. Chem. int. Ed. Engl.*, **19**, 713 (1980).
16. R. W. Saalfrank, W. Paul, P. Schierling, H. Schüler and E. Wilhelm, *Chem. Ber.*, **115**, 57 (1982).
17. H. J. Bestmann, K. Roth and R. W. Saalfrank, *Angew Chem.*, **89**, 915 (1977); *Angew. Chem. int. Ed. Engl.*, **16**, 877 (1977).
18. A. F. Grapov, L. V. Razvodovskaya and N. N. Mel'nikov, *Russ. Chem. Rev.* (*Engl. Transl.*), **50**, 324 (1981).
19. W. Zeiss, *Angew. Chem.*, **88**, 582 (1976); *Angew. Chem. int. Ed. Engl.*, **15**, 555 (1976).
20. T. Kawashima and N. Inamoto, *Bull. Chem. Soc. Jpn.*, **49**, 1924 (1976).
21. J. I. G. Cadogan, J. B. Husband and H. McNab, *J. Chem. Soc., Chem. Commun.*, 1054 (1981).
22. J. I. G. Cadogan, J. B. Husband and H. McNab, *J. Chem. Soc., Perkin Trans. 1*, in press.
23. A. Schmidpeter and J. H. Weinmaier, *Chem. Ber.*, **111**, 2086 (1978).
24. A. Schmidpeter and T. von Criegern, *Angew. Chem.*, **90**, 64 (1978); *Angew. Chem. int. Ed. Engl.*, **17**, 55 (1978).
25. W. S. Sheldrick, D. Schomburg, A. Schmidpeter and T. von Criegern, *Chem. Ber.*, **113**, 55 (1980).
26. A. Schmidpeter, W. Zeiss, D. Schomburg and W. S. Sheldrick, *Angew. Chem.*, **92**, 860 (1980); *Angew. Chem. int. Ed. Engl.*, **19**, 825 (1980).
27. A. Schmidpeter and T. von Criegern, *Chem. Ber.*, **111**, 3747 (1978)
28. W. Storzer, G.-V. Röschenthaler, R. Schmutzler and W. S. Sheldrick, *Chem. Ber.*, **114**, 3609 (1981).
29. A. Schmidpeter and T. von Criegern, *J. Chem. Soc., Chem. Commun.*, 470 (1978).
30. A. Schmidpeter, J. Luber, D. Schomburg and W. S. Sheldrick, *Chem. Ber.*, **109**, 3581 (1976).
31. For example, P. D. Bartlett, D. Mendenhall and D. L. Durham, *J. Org. Chem.*, **45**, 4269 (1980).
32. For a review, see A. G. Rowley in ref. 2, Chap. 7, p. 295.
33. G. Wittig and A. Maercker, *Chem. Ber.*, **97**, 747 (1964).
34. D. Hellwinkel, *Chem. Ber.*, **98**, 576 (1965).
35. D. Hellwinkel and W. Lindner, *Chem. Ber.*, **109**, 1497 (1976).
36. D. Hellwinkel, *Chem. Ber.*, **102**, 528 (1969).

37. D. Hellwinkel and W. Krapp, *Chem. Ber.*, **110**, 693 (1977).
38. C. D. Hall, J. D. Bramblett and F. S. S. Lin, *J. Am. Chem. Soc.*, **94**, 9264 (1972).
39. P. J. Hammond, J. R. Lloyd and C. D. Hall, *Phosphorus and Sulfur*, **10**, 47 (1981).
40. G. Scott, P. J. Hammond, C. D. Hall and J. D. Bramblett, *J. Chem. Soc., Perkin Trans. 2*, 882 (1977); (a) K. C. Caster and L. D. Quin, *Tetrahedron Lett.*, **24**, 5831 (1983).
41. P. J. Hammond, G. Scott and C. D. Hall, *J. Chem. Soc., Perkin Trans. 2*, 205 (1982).
42. D. B. Denney, D. Z. Denney and Y. F. Hsu, *Phosphorus*, **4**, 217 (1974).
43. L. L. Chang, D. Z. Denney, D. B. Denney and Y. F. Hsu, *Phosphorus*, **4**, 265 (1974).
44. D. B. Denney, D. Z. Denney, C. D. Hall and K. L. Marsi, *J. Am. Chem. Soc.*, **94**, 245 (1972).
45. T. J. Katz and E. W. Turnblom, *J. Am. Chem. Soc.*, **92**, 6701 (1970).
46. E. W. Turnblom and T. J. Katz, *J. Am. Chem. Soc.*, **93**, 4065 (1971).
47. E. W. Turnblom and T. J. Katz, *J. Chem. Soc., Chem. Commun.*, 1270 (1972).
48. E. W. Turnblom and T. J. Katz, *J. Am. Chem. Soc.*, **95**, 4292 (1971).
49. K. A. Mesch and L. D. Quin, *Tetrahedron Lett.*, **21**, 4791 (1980).
50. H. Schmidbaur and P. Holl, *Z. Naturforsch., Teil B*, **33**, 489 (1978).
51. B. E. Ivanov, L. A. Valitova, L. A. Kudryavtseva, T. G. Bykova, K. A. Derstuganova and E. I. Gol'dfarb, *Izv. Akad. Nauk SSSR Ser. Khim.*, 672 (1974).
52. B. A. Arbusov, N. A. Polezhaeva and V. V. Smirnov, *Izv. Akad. Nauk SSSR Ser. Khim.*, 686 (1975).
53. I. Granoth, R. Alkabets and E. Shirin, *J. Chem. Soc., Chem. Commun.*, 981 (1981).
54. c.f., D. Hellwinkel and W. Krapp, *Angew Chem.*, **86**, 524 (1974); *Angew. Chem. int. Ed. Engl.*, **13**, 542 (1974).
55. D. Hellwinkel and W. Krapp, *Chem. Ber.*, **111**, 13 (1978).
56. Y. Segall, I. Granoth and A. Kalir, *J. Chem. Soc., Chem. Commun.*, 399 (1975).
57. Y. Segall and I. Granoth, *J. Am. Chem. Soc.*, **100**, 5130 (1978).
58. J. A. Miller and D. Stewart, *J. Chem. Soc., Chem. Commun.*, 156 (1977).
59. For a review, see T. Saegusa, *Angew. Chem.*, **89**, 867 (1977); *Angew. Chem. int. Ed. Engl.*, **16**, 826 (1977).
60. S. Trippett, *Quart. Rev.*, **17**, 406 (1963).
61. W. E. McEwan and A. P. Wolf, *J. Am. Chem. Soc.*, **84**, 676 (1962).
62. W. E. McEwan, A. Bladé-Font and C. A. Vander Werf, *J. Am. Chem. Soc.*, **84**, 677 (1962).
63. R. Huisgen and J. Wulff, *Chem. Ber.*, **102**, 1841 (1969).
64. D. B. Denney, J. J. Vill and M. J. Boskin, *J. Am. Chem. Soc.*, **84**, 3944 (1962).
65. E. Zbiral, *Monatsh. Chem.*, **94**, 78 (1963).
66. A. R. Hands and A. J. H. Mercer, *J. Chem. Soc., (C)*, 1099 (1967).
67. C. T. Eyles and S. Trippett, *J. Chem. Soc. (C)*, 67 (1966).
68. A. R. Hands and A. J. H. Mercer, *J. Chem. Soc. (C)*, 2448 (1968).
69. A. Turcant and M. Le Corre, *Tetrahedron Lett.*, 789 (1977).
70. D. G. Leppard, P. W. Raynolds, C. B. Chapleo and A. S. Dreiding, *Helv. Chim. Acta*, **59**, 695 (1976).
71. E. E. Schweizer and J. G. Liehr, *J. Org. Chem.*, **33**, 583 (1968).
72. E. E. Schweizer, W. S. Creasy, J. G. Liehr, M. E. Jenkins and D. L. Dalrymple, *J. Org. Chem.*, **35**, 601 (1970).
73. W. G. Bentrude and W. D. Johnson, *J. Am. Chem. Soc.*, **90**, 5924 (1968).
74. V. A. Kukhtin and K. M. Kirilova, *Dokl. Akad. Nauk SSSR*, **140**, 835 (1961); [*Chem. Abstr.*, **56**, 4607 (1962)].
75. G. Boekestein, W. G. Voncken, E. H. J. M. Jansen and H. M. Buck, *Recl. Trav. Chim. Pays-Bas*, **93**, 69 (1974).
76. W. B. Bentrude, *J. Chem. Soc., Chem. Commun.*, 174 (1967).
77. R. F. C. Brown, *Pyrolytic Methods in Organic Chemistry*, Academic Press, New York (1980).
78. T. Mukaiyama, H. Nambu and T. Kumamoto, *J. Org. Chem.*, **29**, 2243 (1964).
79. T. Mukaiyama, H. Nambu and M. Okamoto, *J. Org. Chem.*, **27**, 3651 (1962).
80. P. Yates, *J. Am. Chem. Soc.*, **74**, 5376 (1952).
81. T. Mukaiyama and T. Kumamoto, *Bull. Chem. Soc. Jpn.*, **39**, 879 (1966) [*Chem. Abstr.*, **65**, 7085 (1966)].
82. D. Bernard and R. Burgada, *Tetrahedon Lett.*, 3455 (1973).
83. Y. A. Levin, I. P. Gozman and S. G. Salikhov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2609 (1968) [*Chem. Abstr.*, **70**, 68269 (1969)].
84. N. J. De'Ath and D. B. Denney, *J. Chem. Soc., Chem. Commun.*, 395 (1972).
85. R. Schwarz and I. Ugi, *Angew. Chem.*, **93**, 836 (1981); *Angew. Chem. int. Ed. Engl.*, **20**, 789 (1981).
86. A. N. Pudovik, É. S. Batyeva and V. D. Nesterenko, *Zh. Obshch. Khim.*, **44**, 1411 (1974).
87. D. B. Denney, D. Z. Denney and G. DiMiele, *Phosphorus and Sulfur*, **4**, 125 (1978).
88. A. Skowrońska, J. Mikołajczak and J. Michalski, *J. Chem. Soc., Chem. Commun.*, 791 (1975).

89. W. Gerrard and W. J. Green, *J. Chem. Soc.*, 2550 (1951).
90. J. Michalski, J. Mikołajczak, M. Pakulski and A. Skowrońska, *Phosphorus and Sulfur*, **4**, 233 (1978).
91. D. B. Denney and D. H. Jones, *J. Am. Chem. Soc.*, **91**, 5821 (1969).
92. F. Ramirez, A. S. Gulati and C. P. Smith, *J. Org. Chem.*, **33**, 13 (1968).
93. J. H. Boyer and R. Selvarajan, *J. Org. Chem.*, **35**, 1229 (1970).
94. M. Willson, R. Burgada and F. Mathis, *Bull. Soc. Chim. Fr.*, 2241 (1975).
95. I. V. Konovalova, T. V. Yudina, E. K. Ofitserova, N. P. Anoshina and A. N. Pudovik, *Zh. Obshch, Khim.*, **48**, 1936 (1978) [*Chem. Abstr.*, **90**, 38843 (1979)].
96. R. Boigegrain and B. Castro, *Tetrahedron*, **32**, 1283 (1976).
97. P. D. Bartlett, A. L. Baumstark and M. E. Landis, *J. Am. Chem. Soc.*, **95**, 6486 (1973).
98. F. Ramirez, S. B. Bhatia and C. P. Smith, *Tetrahedron*, **23**, 2067 (1967).
99. D. E. Bissing and A. J. Speziale, *J. Am. Chem. Soc.*, **87**, 1405 (1965).
100. P. D. Bartlett, M. E. Landis and M. J. Shapiro, *J. Org. Chem.*, **42**, 1661 (1977).
101. J. Koo and G. B. Schuster, *J. Am. Chem. Soc.*, **99**, 5403 (1977).
102. B. C. Chang, W. E. Conrad, D. B. Denney, D. Z. Denney, R. Edelman, R. L. Powell and D. W. White, *J. Am. Chem. Soc.*, **93**, 4004 (1971).
103. A. M. Baumstark, C. J. McCloskey, T. E. Williams and D. R. Chrisope, *J. Org. Chem.*, **45**, 3593 (1980).
104. See also A. M. Baumstark, M. Barrett and K. M. Kral, *J. Heterocycl. Chem.*, **19**, 201 (1982).
105. H. Germa and R. Burgada, *Bull. Soc. Chim. Fr.*, 2607 (1975).
106. A. P. Stewart and S. Trippett, *J. Chem. Soc., Chem. Commun.*, 1279 (1970).
107. F. Ramirez and C. P. Smith, *J. Chem. Soc., Chem. Commun.*, 662 (1967).
108. (a) I. J. Borowitz, P. D. Readio and P. Rusek, *J. Chem. Soc., Chem. Commun.*, 240 (1968); (b) I. J. Borowitz, M. Anschel and P. D. Readio, *J. Org. Chem.*, **36**, 553 (1971).
109. I. J. Borowitz and M. Anschel, *Tetrahedron Lett.*, 1517 (1967).
110. A. C. Poshkus and J. E. Herweh, *J. Org. Chem.*, **29**, 2567 (1964).
111. H.-G. Henning, *Tetrahedron Lett.*, 2585 (1966).
112. T. Mukaiyama, T. Kumamoto and T. Nagaoka, *Tetrahedron Lett.*, 5563 (1966).
113. F. Ramirez, S. B. Bhatia, A. V. Patwardhan and C. P. Smith, *J. Org. Chem.*, **32**, 3547 (1967).
114. F. Ramirez and N. Ramanathan, *J. Org. Chem.*, **26**, 3041 (1961).
115. F. Ramirez, N. Ramanathan and N. B. Desai, *J. Am. Chem. Soc.*, **84**, 1317 (1962).
116. W. G. Bentrude and K. R. Darnall, *J. Chem. Soc., Chem. Commun.*, 862 (1969).
117. F. Ramirez, C. P. Smith and J. F. Pilot, *J. Am. Chem. Soc.*, **90**, 6726 (1968).
118. M. Ul-Haque, C. N. Caughlan, F. Ramirez, J. F. Pilot and C. P. Smith, *J. Am. Chem. Soc.*, **93**, 5229 (1971).
119. R. Burgada, *Bull. Soc. Chim. Fr.*, 407 (1975).
120. A. Munoz, B. Garrigues and M. Koenig, *Tetrahedron*, **36**, 2467 (1980).
121. R. Sarma, F. Ramirez, B. McKeever, M. Nowakowski and J. F. Marecek, *J. Am. Chem. Soc.*, **100**, 5391 (1978).
122. D. Schomburg, W. Storzer, R. Bohlen, W. Kuhn and G.-V. Röschenthaler, *Chem. Ber.*, **116**, 3301 (1983).
123. J. A. Gibson and G.-V. Röschenthaler, *J. Chem. Soc., Chem. Commun.*, 694 (1974).
124. J. A. Gibson, G.-V. Röschenthaler, D. Schomburg and W. S. Sheldrick, *Chem. Ber.*, **110**, 1887 (1977).
125. W. Storzer, G.-V. Röschenthaler, R. Schmutzler and W. S. Sheldrick, *Chem. Ber.*, **114**, 3609 (1981).
126. E. M. Rokhlin, Y. V. Zeifman, Y. A. Cheburkov, N. P. Gambaryan and I. L. Knunyants, *Dokl. Akad. Nauk SSSR*, **161**, 1356 (1965) [*Chem. Abstr.*, **63**, 4153 (1965)].
127. F. Ramirez, J. F. Pilot, C. P. Smith, S. B. Bhatia and A. S. Gulati, *J. Org. Chem.*, **34**, 3385 (1969).
128. F. Ramirez, C. P. Smith, J. F. Pilot and A. S. Gulati, *J. Org. Chem.*, **33**, 3787 (1968).
129. E. Duff, D. R. Russell and S. Trippett, *Phosphorus*, **4**, 203 (1974).
130. J. A. Gibson, G.-V. Röschenthaler, K. Sauerbrey and R. Schmutzler, *Chem. Ber.*, **110**, 3214 (1977).
131. V. Mark, *J. Am. Chem. Soc.*, **85**, 1884 (1963).
132. G. W. Griffin, D. M. Gibson and K. Ishikawa, *J. Chem. Soc., Chem. Commun.*, 595 (1975).
133. H. J. Bestmann and R. Kunstmann, *Angew. Chem.*, **78**, 1059 (1966); *Angew. Chem. int. Ed. Engl.*, **5**, 1039 (1966).
134. H. J. Bestmann and R. Kunstmann, *Chem. Ber.*, **102**, 1816 (1969).
135. R. Huisgen and J. Wulff, *Tetrahedron Lett.*, 917 (1967).
136. R. Huisgen and J. Wulff, *Chem. Ber.*, **102**, 1833 (1969).
137. See also G. Gaudiano, R. Mondelli, P. P. Ponti, C. Ticozzi and A. Umani-Ronchi, *J. Org. Chem.*, **33**, 4431 (1968).
138. A. Hassner and V. Alexanian, *J. Org. Chem.*, **44**, 3861 (1979).
139. A. Padwa, J. K. Rasmussen and A. Tremper, *J. Am. Chem. Soc.*, **98**, 2605 (1976).
140. H. J. Bestmann, T. Denzel, R. Kunstmann and J. Lengyel, *Tetrahedron Lett.*, 2895 (1968).

141. O. Tsuge, H. Watanabe and Y. Kiryu, *Bull. Chem. Soc. Jpn.*, **52**, 3387 (1979).
142. O. Tsuge, H. Watanabe and Y. Kiryu, *Bull. Chem. Soc. Jpn.*, **52**, 3654 (1979).
143. O. Tsuge, T. Ohnishi and H. Watanabe, *Heterocycles*, **16**, 2085 (1981).
144. T. Sasaki, T. Yoshioka and Y. Suzuki, *Yuki Gosei Kagaku Kyokai Shi*, **28**, 1054 (1970) [*Chem. Abstr.*, **74**, 125528 (1971)].
145. G. L'Abbe, J.-M. Borsus, P. Ykman and G. Smets, *Chem. Ind.* (*London*), 1491 (1971).
146. J. I. G. Cadogan, R. A. North and A. G. Rowley, *J. Chem. Res.* (S) 1; (M) 0178 (1978).
147. R. D. Gareev, G. M. Loginova and A. N. Pudovik, *Zh. Obshch. Khim.*, **46**, 1906 (1976). [*Chem. Abstr.*, **85**, 177553 (1976)].
148. R. D. Gareev, G. M. Loginova, Y. Y. Samitov and A. N. Pudovik, *Zh. Obshch. Khim.*, **47**, 2663 (1977). [*Chem. Abstr.*, **88**, 135852 (1978)].
149. W. E. Krueger, M. B. McLean, A. Rizwaniuk, J. R. Maloney, G. L. Behelfer and B. E. Boland, *J. Org. Chem.*, **43**, 2877 (1978).
150. J. Wulff and R. Huisgen, *Angew. Chem.*, **79**, 472 (1967); *Angew. Chem. int. Ed. Engl.*, **6**, 457 (1967).
151. R. Huisgen and J. Wulff, *Chem. Ber.*, **102**, 746 (1969).
152. K. Burger, J. Albanbauer and F. Manz, *Chem. Ber.*, **107**, 1823 (1974).
153. K. Burger and J. Fehn, *Angew. Chem.*, **83**, 761 (1971); *Angew. Chem. int. Ed. Engl.*, **10**, 728 (1971).
154. K. Burger and J. Fehn, *Angew. Chem.*, **83**, 762 (1971); *Angew. Chem. int. Ed. Engl.*, **10**, 729 (1971).
155. K. Burger and J. Fehn, *Chem. Ber.*, **105**, 3814 (1972).
156. K. Burger, K. Einhellig, W.-D. Roth and L. Hatzelmann, *Tetrahedron Lett.*, 2701 (1974).
157. K. Burger, W.-D. Roth, K. Einhellig and L. Hatzelmann, *Chem. Ber.*, **108**, 2737 (1975).
158. K. Burger and K. Einhellig, *Chem. Ber.*, **106**, 3421 (1973).
159. K. Burger and W.-D. Roth, *Synthesis*, 731 (1975).
160. K. Burger, S. Tremmel, W.-D. Roth and H. Goth, *J. Heterocycl. Chem.*, **18**, 247 (1981).
161. K. Burger and J. Fehn, *Angew. Chem.*, **84**, 35 (1972); *Angew. Chem. int. Ed. Engl.*, **11**, 47 (1972).
162. K. Burger, J. Fehn and E. Müller, *Chem. Ber.*, **106**, 1 (1972).
163. K. Burger, W.-D. Roth and K. Neumayr, *Chem. Ber.*, **109**, 1984 (1976).
164. K. Burger, K. Einhellig, W.-D. Roth and E. Daltrozzo, *Chem. Ber.*, **110**, 605 (1977).
165. A. Padwa, P. H. J. Carlsen and A. Ku, *J. Am. Chem. Soc.*, **100**, 3494 (1978).
166. K. Burger, J. Fehn and E. Moll, *Chem. Ber.*, **104**, 1826 (1971).
167. K. Burger, K. Einhellig, G. Süss and A. Gieren, *Angew. Chem.*, **85**, 169 (1973); *Angew. Chem. int. Ed. Engl.*, **12**, 156 (1973).
168. K. Burger, R. Ottlinger, H. Goth and J. Firl, *Chem. Ber.*, **113**, 2699 (1980), and references therein.
169. K. Burger, E. Burgis and P. Holl, *Synthesis*, 816 (1974).
170. R. Kober and W. Steglich, *Justus Liebigs Ann. Chem.*, 599 (1983).
171. J. I. G. Cadogan, J. B. Husband and H. McNab, *J. Chem. Soc., Perkin Trans. 2*, 697 (1983).
172. J. I. G. Cadogan, J. B. Husband and H. McNab, *J. Chem. Soc., Perkin Trans. 1*, 1489 (1983).
173. J. I. G. Cadogan and B. S. Tait, *J. Chem. Soc., Perkin Trans. 1*, 2396 (1975).
174. J. I. G. Cadogan and N. J. Tweddle, *J. Chem. Soc., Perkin Trans. 1*, 1278 (1979).
175. H. B. Stegmann, R. Haller, A. Burmester and K. Scheffler, *Chem. Ber.*, **114**, 14 (1981).
176. K. Scheffler, A. Burmester, R. Haller and H. B. Stegmann, *Chem. Ber.*, **114**, 23 (1981).
177. For example: S. A. Terent'eva, M. A. Pudovik and A. N. Pudovik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2185 (1978): [*Chem. Abstr.*, **90**, 23186 (1979)].
178. R. Appel and R. Halstenberg, *Chem. Ber.*, **109**, 814 (1976).
179. See Y. Ittah, Y. Sasson, I. Shahak, S. Tsaroom and J. Blum, *J. Org. Chem.*, **43**, 4271 (1978) for a related reaction.
180. A. Schmidpeter and T. von Criegern, Chem. Ber., **112**, 2762 (1979).
181. R. Huisgen and J. Wulff, *Tetrahedron Lett.*, 921 (1967).
182. R. Huisgen and J. Wulff, *Chem. Ber.*, **102**, 1848 (1969).
183. E. v. Hinrichs and I. Ugi, *J. Chem. Res.*, (S) 338; (M) 3973 (1978).
184. A. Schmidpeter and J. Luber, *Chem. Ber.*, **108**, 820 (1975).
185. C. C. Walker and H. Shechter, *J. Am. Chem. Soc.*, **90**, 5626 (1968).
186. J.-P. Majoral, R. Kraemer, T. N'gando M'pondo and J. Navech, *Tetrahedron Lett.*, **21**, 1307 (1980).
187. W. Adam, R. J. Ramirez and S.-C. Tsai, *J. Am. Chem. Soc.*, **91**, 1254 (1969).
188. W. Adam and A. Rios, *J. Org. Chem.*, **36**, 407 (1971).
189. W. Adam and J. W. Diehl, *J. Chem. Soc., Chem. Commun.*, 797 (1972).
190. Y. Kimura, T. Kokura and T. Saegusa, *J. Org. Chem.*, **48**, 3815 (1983).