

The Organic Chemistry of Phospholes

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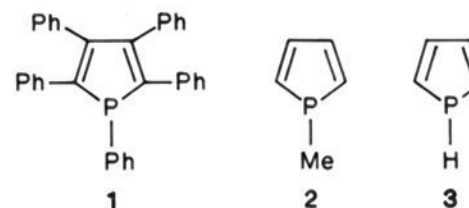
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François Mathey is Professor of Chemistry at Ecole Polytechnique—Palaiseau near Paris (France). He was born in Paris in 1941, studied in Ecole Polytechnique from 1961 to 1963, and then received a Ph.D. in Organic Chemistry from the University of Paris VI in 1971. He was appointed group leader in Institut National de Recherche Chimique Appliquée (IRCHA) in 1969, left IRCHA for Société Nationale des Poudres et Explosifs (SNPE) in 1980, and, finally, joined the faculty at Ecole Polytechnique in 1987. His research deals with organophosphorus and transition-metal chemistry.

criteria presently in use for defining the controversial notion of heteroaromaticity have been established or checked with them.

In view of such an extensive field of research, the chemistry of phospholes seems rather limited. This reflects a general underdevelopment of phosphorus heterocyclic chemistry when compared to its nitrogen, oxygen, and sulfur counterparts. In fact, the first phosphole **1** has been discovered as late as 1959 by two independent groups.^{1,2} In the same vein, the first C-unsubstituted phosphole **2** was only prepared in 1967³ and the parent molecule **3** was characterized for the first



time at low temperature as recently as 1983.⁴ The relatively immature state of phosphole chemistry is therefore not very surprising. However, it can be confidently stated here that it is now put on a firm ground since some initial misinterpretations have been recently corrected. Thus, a review on this field appears all the more timely since even the most recent among the numerous older reviews partly or fully devoted to the same topic⁵⁻¹³ need to be extensively completed.

Benzo-annelated phospholes have been excluded from this review because they do not contain a free dienic system and do not behave as typical phospholes for that reason. Phosphole complexes have been comprehen-

Introduction

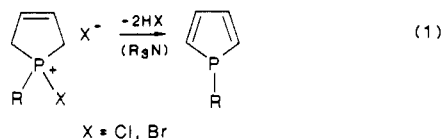
Five-membered heterocycles such as pyrroles, furans, and thiophenes together with six-membered pyridines and a restricted number of other species form the backbone of classical heterocyclic chemistry. Since their discovery in the course of the 19th century, their chemistry has been continuously developed and now reaches huge proportions. These cycles are essential to life as illustrated by the key biological roles of porphyrin and porphyrin-like metal complexes such as hemoglobin, chlorophyll, and vitamin B₁₂. The recent discovery of the electroconducting properties of doped films of polypyrrole and polythiophene adds a new dimension to their applied chemistry. On another side, pyrrole, furan, and thiophene are typical representatives of the so-called "aromatic" heterocycles and most of the

sively covered elsewhere¹⁴⁻¹⁷ and are also excluded except when complexation is used as a tool to promote a new reaction at the ring. The literature has been searched up to the end of 1986.

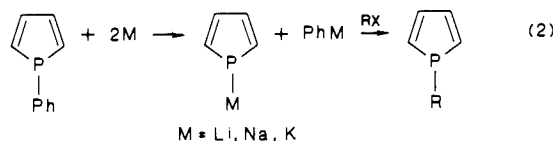
I. Synthetic Problems

A. Building the 1*H*-Phosphole Ring

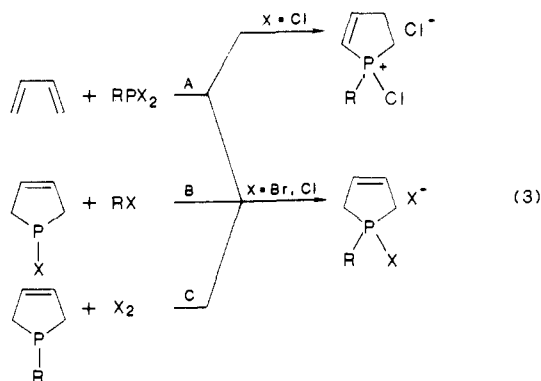
By far the simplest and most versatile synthesis of phospholes has been initially proposed by Mathey in 1969.¹⁸ It relies on the dehydrohalogenation of 1-halophospholenium halides by tertiary amines (eq 1).



In its original version, the reaction was run in boiling benzene with a very strong base (DBU). A first improvement¹⁹ was to replace benzene by a mixture of hydrocarbon (benzene, hexane, etc.) and dichloromethane. In such media, halophospholenium halides are partly soluble so that the reaction can be carried out between 0 °C and room temperature. The yields and the purities of the phospholes thus obtained are much better than in the previous case. The final improvement²⁰ was to replace DBU by other amines such as α -picoline or *N*-methylimidazole, which are both cheaper, easier to dry, and somewhat more efficient. The scope of this reaction is well illustrated in Table I. When R is phenyl, the yields are often quite high. This has allowed 1-phenyl-3,4-dimethylphosphole to be produced up to the 30-kg scale by the optimized technique which has been patented.³¹ Conversely, the yields are often much lower for 1-alkyl derivatives. This is due to their higher instability and susceptibility to oxidation. In that case, it is better to use a phenyl to alkyl exchange according to eq 2 (see Section I.C).



The starting halophospholenium halides can be produced through three different routes, which are summarized in eq 3. Route A is the well-known McCor-



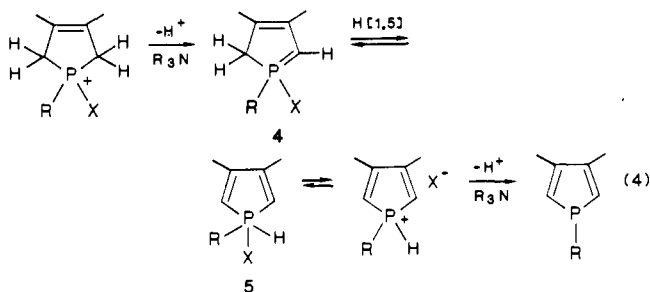
mack reaction, the scope of which has been thoroughly discussed in ref 11. When X = Cl, this cycloaddition sometimes produces halo-2-phospholenium salts, which

TABLE I. Synthesis of Phospholes by Dehydrohalogenation of 1-Halophospholenium Halides

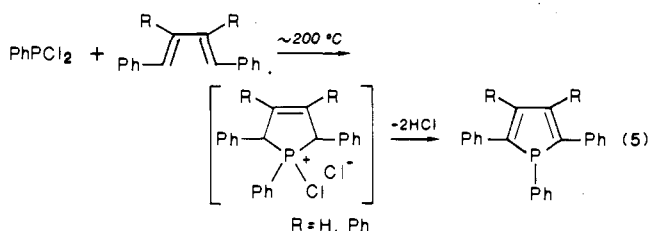
nucleus	R, yield (ref)
	Ph, 50% (20); <i>n</i> -Bu, 14% (21)
	Ph, 75% (20); PhCH ₂ , 7.4% (24); Me, 12% (24); <i>n</i> -Bu, 8% (21)
	Ph, 15% (25); Me, 14% (24)
	Me, 23% (24, 26)
	Ph, 86% (20); PhCH ₂ , 75% (20); Me, 30% (20); <i>n</i> -Bu, 18% (21); <i>n</i> -C ₁₂ H ₂₅ , 33% (22); MeOCH ₂ , 36% (23); MeSCH ₂ , 32% (23); NCCH ₂ CH ₂ , 15% (23)
	Me, 23% (24)
	Ph, 25% (27); Me, 18% (27)
	PhCH ₂ (28)
	Ph, 40% (27); Me, 20% (27)
	Ph, 38% (29)
	Ph, 50% (30)

are unsuitable for the phosphole synthesis.³² Routes B and C have been proposed by Quin.²⁴ The most noteworthy illustration of route B is the synthesis of some phospholes with functional groups at phosphorus.²³ Route C has served *inter alia* for the synthesis of some phospholecarboxylates^{24,26} and of a very interesting 2,2'-biphosphole.³⁰

The most likely mechanism of this phosphole synthesis is depicted in eq 4. The key step is a reversible hydrogen [1,5] sigmatropic shift, which is responsible for an equilibrium between the cyclic ylide 4 and the covalent form of the phospholium salt 5. Whereas it is difficult to prove such a mechanism, it has been possible to perform the reverse reaction, i.e., the conversion of the phosphole into the corresponding halophospholenium salt by addition of two molecules of HX, and to demonstrate the initial protonation at phosphorus leading to 5 by ³¹P NMR (see Section III.A.1).

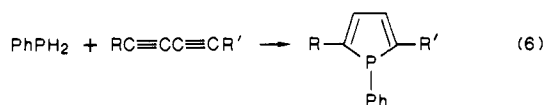


Directly related to the previous method but discovered earlier is the synthesis of 1,2,5-triphenyl- and 1,2,3,4,5-pentaphenylphospholes by the straightforward reaction of PhPCl_2 with 1,4-diphenyl- and 1,2,3,4-tetraphenylbutadienes at high temperatures^{33,34} (eq 5).



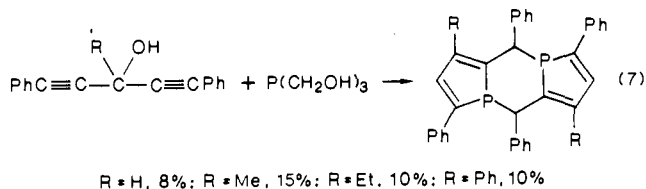
The technique has been recently improved by using boiling PhPCl_2 as the reaction medium. Yields as high as 70% of 1,2,5-triphenylphosphole have thus been obtained.³⁵ The mechanism very likely involves the thermal dehydrohalogenation of a transient halophospholenium halide. One of the possible driving forces is probably the appearance of some electronic delocalization between the phenyl C_2 and C_5 substituents through the dienic system created when the phospholene is converted into the phosphole nucleus. In line with this, the attempted synthesis of 1,3,4-triphenylphosphole by this route has failed.³⁶ On the other hand, attempted generalizations³⁷ in which PhPCl_2 was replaced by other arylchlorophosphines have failed too due to some scrambling between the aryl on phosphorus and the phenyls on the dienes. Aryl [1,5] sigmatropic shifts around the phosphole nucleus are at the origin of this scrambling (see Section I.B).

A more classical route to phospholes has been proposed by Märkl.³⁸ It relies on the cycloaddition of primary phosphines with 1,3-diyne (eq 6). The re-



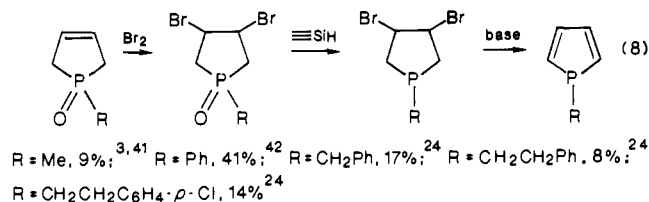
R = R' = Ph, 60-76%;^{38,39} R = R' = Me, 51%;³⁸ R = R' = naphthyl, 89%;³⁸ R = R' = *p*-tolyl, 59%;³⁸ R = R' = *p*-BrC₆H₄, 16%;³⁸ R = Me, R' = Ph, 30%;⁴⁰ R = Me, R = CH₂CH₂Ph, 70%;⁴⁰ R = Me₂CH, R' = Ph, 86%⁴⁰

action is catalyzed by BuLi, PhLi, CuCl, KOH, or AIBN. Its main drawback is its limitation to the synthesis of 1,2,5-trisubstituted phospholes. The cycloaddition of phosphines with diynes also forms the basis of a low-yield synthesis of some very peculiar tricyclic phospholes⁵⁰ (eq 7). The only other route to trivalent phospholes that has some generality was proposed by Quin, who used it to prepare the first C-unsubstituted phosphole³ (eq 8). Due to its complexity and its low



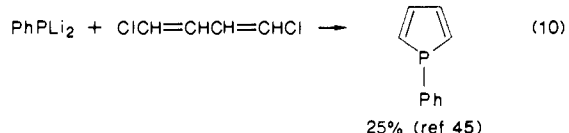
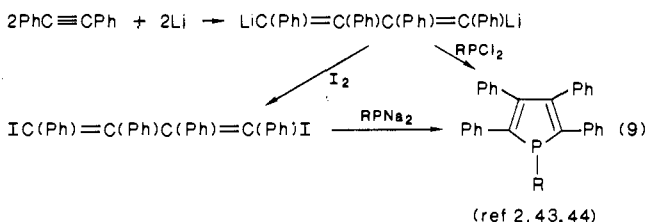
R = H, 8%; R = Me, 15%; R = Et, 10%; R = Ph, 10%

overall yields, this method now has mainly an historical interest.

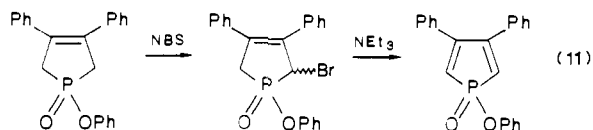


R = Me, 9%;^{3,41} R = Ph, 41%;⁴² R = CH₂Ph, 17%;²⁴ R = CH₂CH₂Ph, 8%;²⁴ R = CH₂CH₂C₆H₄-*p*-Cl, 14%²⁴

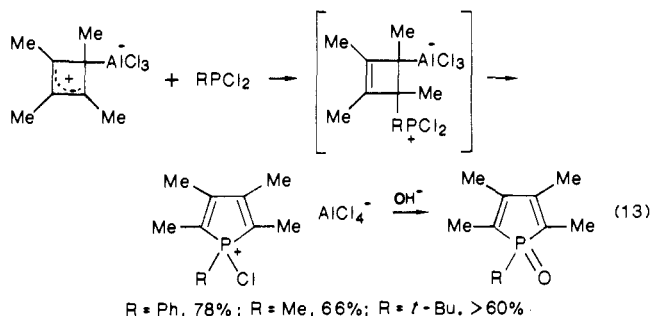
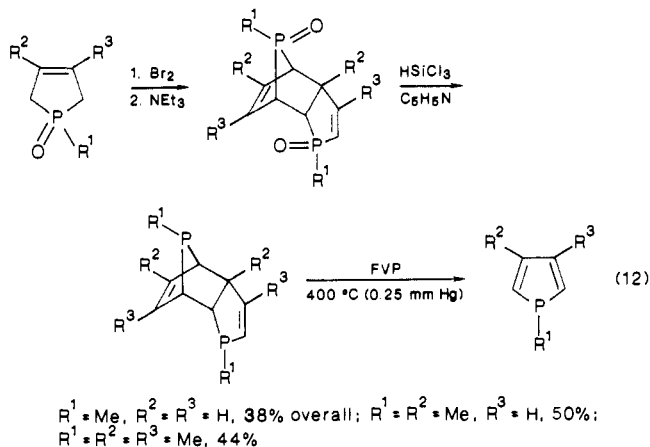
Finally, another approach with a very limited applicability but still in use today because of its convenience relies on the condensation of a 1,4-dithiobutadiene with a dihalophosphine or, conversely, of a 1,4-dihalobutadiene with a dilithio- or a disodio-phosphine (eq 9 and 10).



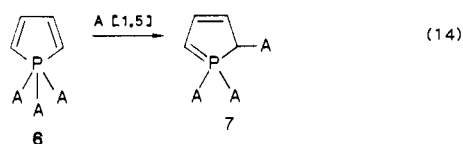
The phosphole nucleus has also been built in its *P*-oxide version. The basic drawback of this kind of approach is that phosphole oxides normally dimerize except when they are heavily substituted at the ring (this topic is discussed in Section III.A.4). Thus, such methods have often been used to generate transient monomeric phosphole oxides for further reactions. The classical scheme relies on a combined bromination-dehydrobromination of the easily available phospholene oxides. The sequence depicted in eq 11 yields a stable monomeric phosphole oxide.⁴⁶ It must be noted here



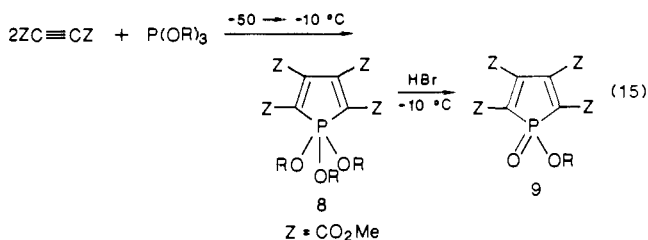
that it is possible in some instances to convert a phosphole dimer back into the corresponding monomer by a thermal retro-Diels-Alder reaction as exemplified in eq 12.^{47,48} A brand new and efficient synthesis of pentasubstituted phosphole oxides has also been proposed recently by Hogeveen.⁴⁹ It involves the reaction of a dihalophosphine with a cyclobutadiene- AlCl_3 σ -complex (eq 13). This kind of complex is obtained by dimerization of alkynes in the presence of AlCl_3 .



The phosphole ring can also be built as a phosphorane. The basic problem of this kind of approach is that, in a phosphorane such as 6, the A group has a strong tendency to migrate from phosphorus to carbon. This type of [1,5] sigmatropic shift leading to a 2*H*-phosphole like 7 (eq 14) is discussed in Section I.B. In

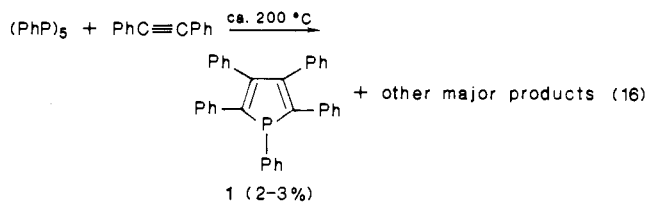


order to freeze out this kind of shift, it is necessary to use A groups that are strongly bonded to phosphorus. Alkoxy groups have proven to be suitable. The proposed scheme (eq 15) involves the reaction of trialkyl phosphites with dimethyl acetylenedicarboxylate.⁵¹⁻⁵³

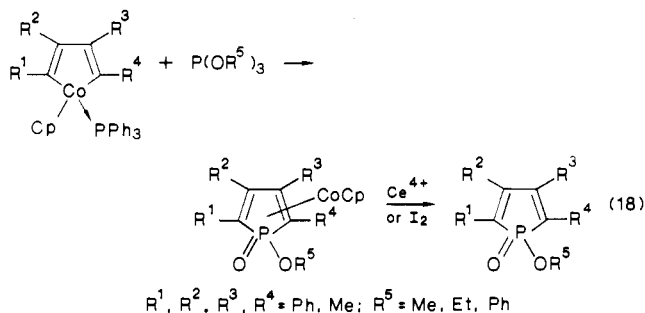
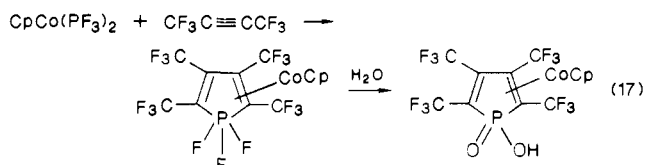


The stability of 8 is especially high when a cyclic phosphite is used in the reaction.⁵³ Treatment of 8 by dry HBr in diethyl ether induces a dealkylation yielding the stable phosphole oxide 9. The sequence can be repeated with alkyl- or arylphosphonites leading to phosphole oxides in which *P*-OR are replaced respectively by *P*-alkyl or *P*-aryl groups.⁵⁴ From another standpoint, it is difficult not to draw a parallel between the reaction leading to 8 and the formation of traces of 1 in the reaction of tolan with pentaphenylcyclopentaphosphine⁵⁵ (eq 16).

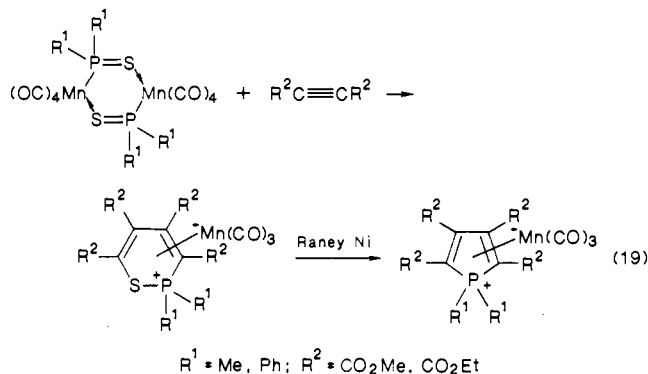
Finally, the phosphole ring has also been built in the coordination spheres of various transition metals. The



first example has been described by Barrow et al.^{56,57} (eq 17). More recently, Yasufuku et al.⁵⁸ proposed another more general route using cobalt (eq 18). Almost



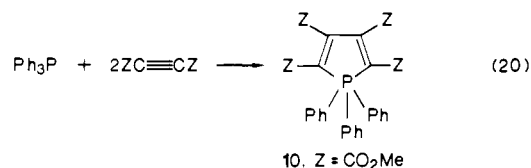
simultaneously, Lindner et al.^{59,60} described a third example with manganese (eq 19). In all cases, the



phosphole dienic system is (at least initially) η^4 -bonded to the transition metal and the phosphorus atom outside of the coordination sphere. All the structures have been checked by X-ray analysis.

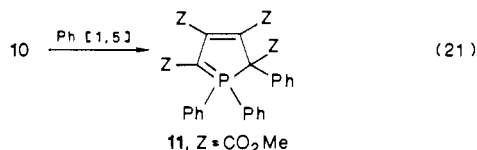
B. 2*H*- and 3*H*-Phospholes and the 1*H*- \rightleftharpoons 2*H*-Phosphole Equilibrium

The story of 2*H*-phospholes started very early only 2 years after the discovery of the first 1*H*-phosphole 1. However, the beginnings were quite confusing. In 1961, Johnson and Tebby⁶¹ together with another group⁶² stated that the reaction of triphenylphosphine with dimethyl acetylenedicarboxylate afforded a penta-coordinate phosphole 10 (eq 20). Ten years later,

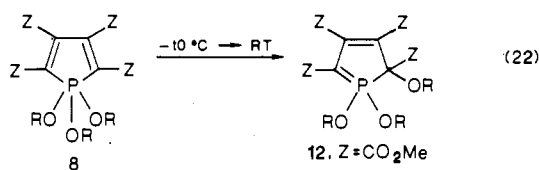


Tebby,^{63,64} after having completed a careful study of the

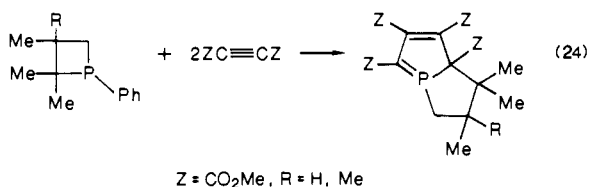
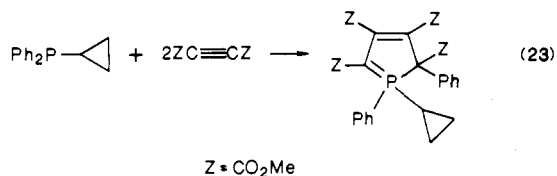
various species involved in this reaction, established that phosphole 10 was only an unstable intermediate rearranging rapidly at low temperature into the corresponding ylide 11 (eq 21). The intramolecular nature



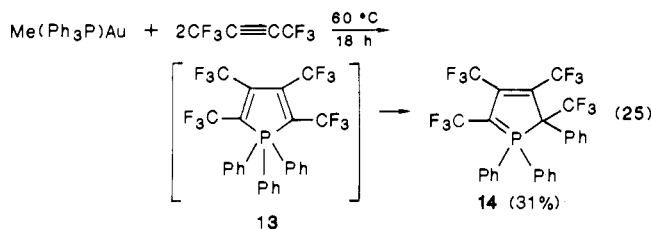
of the phenyl migration leading to 11 was established by allowing a mixture of triphenyl- and tri-*p*-tolylphosphines to react with acetylenedicarboxylate. Only triphenyl- and tri-*p*-tolyl-2*H*-phospholes were thus obtained.⁶⁴ Much more recently a similar sequence was established with trialkyl phosphites as already mentioned earlier (eq 15). The 1,1,1-trialkoxyposphole 8 is stable up to -10 °C but then rearranges like 10 to give a 2*H*-phosphole 12^{51,52} (eq 22, RT = room temperature).



The chemistry described in eq 20–22 seems to have some generality. It was repeated with cyclopropyldiphenylphosphine⁶⁵ (eq 23) and with some phosphetanes⁶⁶ (eq 24). It is interesting to note that the order

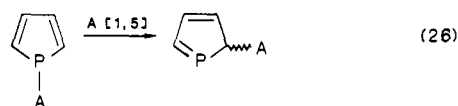


of migrating ability is CMe₂ (phosphetane) > Ph > cyclopropyl. The cyclic strain of the four-membered ring explains why the sp³ P-substituent migrates more readily than the phenyl in reaction 24. On the other hand, the reaction of a triphenylphosphine-gold complex with hexafluorobutyne was reported by Stone,⁶⁷ who assigned the phosphorane structure 13 to the reaction product (eq 25). However, the inequivalency of

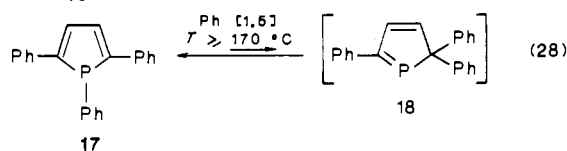
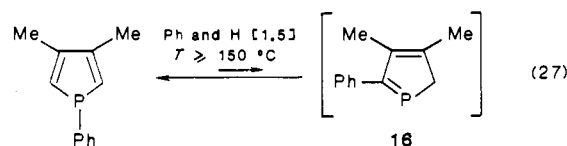


the four CF₃ groups suggests that the ylidic structure 14 is the correct one. The spontaneous transformation of the nonaromatic phosphoranes 8, 10, and the like into the corresponding cyclic ylides is not very surprising since phosphorus is well-known to have a tendency to reduce its coordination number from 5 to 4. On the

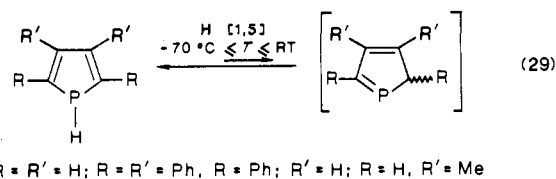
contrary, similar transformation occurring with tervalent phospholes (eq 26) appeared completely unlikely



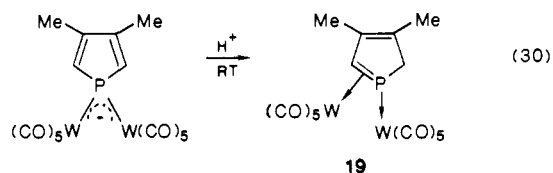
before its unexpected discovery. Indeed, the migration of the P-substituent from P to C reduces the coordination number of phosphorus from 3 to 2 contrary to the normal tendency and suppresses the weak aromatic stabilization of the phosphole ring. Thus, the discovery in 1981 of the equilibria displayed in eq 27 and 28 came as a shock.⁶⁸ The dicoordinated 2*H*-phospholes 16 and



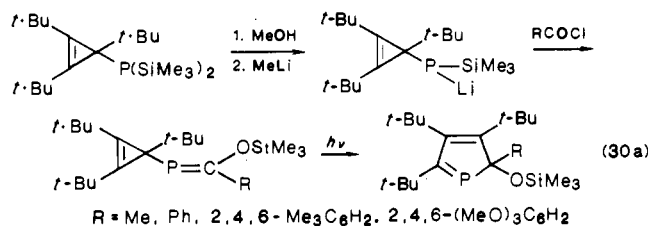
18 are, of course, unstable and highly reactive species. They were identified through their reactions with various trapping reagents (their reactivity is discussed in Section III.B). Sometime later, a similar transformation involving P-unsubstituted phospholes was put in evidence^{4,69} (eq 29). These equilibria occur at low tem-



peratures. Subsequently, it proved possible to obtain a stable 2*H*-phosphole complex by carrying out the same transformation in the coordination sphere of tungsten⁷⁰ (eq 30). The formula of 19 was checked by



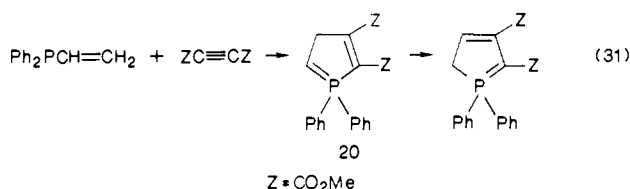
X-ray crystal structure analysis. Even more recently, it was finally possible to obtain stable 2*H*-phospholes by the route depicted in eq 30a.^{70a}



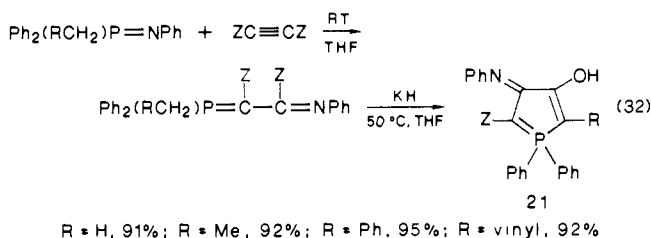
The mechanism of all these 1*H*- ⇌ 2*H*-phosphole interconversions was discussed by Mathey.⁴ In a pentacoordinate, tetracoordinate, or tricoordinate phosphole, one exocyclic P-A bond always forms an angle close to 90° with the plane of the dienic system. Thus,

some overlap occurs between the σ orbital of the P-A bond and the π^* empty orbital of the dienic system. This two-electron stabilizing interaction (hyperconjugation) allows the classical [1,5] sigmatropic shifts to take place. These concerted intramolecular shifts are responsible for the $1H \rightleftharpoons 2H$ -phosphole interconversions. They are easier if the P-A bond is weaker, thus explaining the following order of migrating ability $H \gg Ph \gg OR$. They are easier if the diene-P-A bond angle is closer to 90° (better σ, π^* overlap), thus explaining why the migration takes place more easily in a phosphorane (with a diequatorial phosphole ring, this angle is very close to 90°) than in a trivalent phosphole (this angle is close to 67° ; see ref 71) or in a tetracoordinate phosphole (one such shift has been demonstrated with the P-sulfide of phosphole 15; see ref 68).

$3H$ -Phospholes are much less known than $2H$ -phospholes. Such a species was first invoked by Hughes^{72,73} in the reaction of vinylidiphosphine with dimethyl acetylenedicarboxylate (eq 31). Ylide



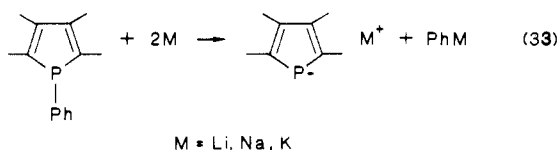
20 is unstable and very reactive. It can be trapped before tautomerization can occur by *p*-nitrobenzaldehyde (Wittig reaction) or by an excess of acetylenedicarboxylate (formal [4 + 2] cycloaddition). Much more recently, stable $3H$ -phospholes were finally described by Barluenga et al. in a preliminary communication⁷⁴ (eq 32). Compounds **21** are stable, high-



melting solids whose formulae were unambiguously established by ¹H and ¹³C NMR spectroscopy. Their chemistry is not described yet.

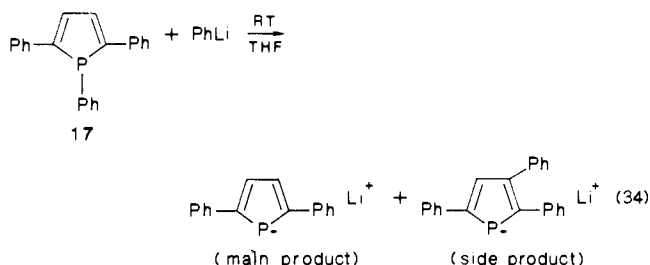
C. Synthesis of the Phospholyl Anions

The phospholyl anions have been discovered by Braye.³⁹ The initial synthesis is still the only practical route to these species. It involves the cleavage by alkali metals of the phosphorus-phenyl bond of 1-phenylphospholes (eq 33). The selectivity and readiness of

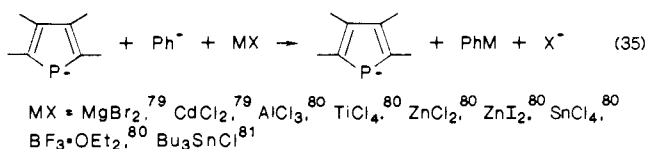


this cleavage are certainly due to the strong driving force provided to the reaction by the additional electronic delocalization occurring within the phosphole ring when the weakly aromatic phosphole is converted into the highly aromatic phospholyl anion. The reaction is generally carried out at room temperature in THF.

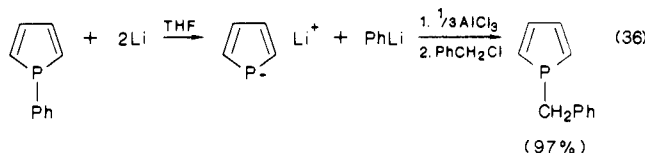
The phenyl P-substituent may be replaced by any other group including alkyl groups. The mechanism of this cleavage has been investigated by ESR.⁷⁵⁻⁷⁷ It involves, first, a mono-electronic reduction yielding a phosphole radical anion which is probably partly stabilized by delocalization of the unpaired electron over the ring. Above ca. -30°C , this radical collapses, releasing a phenyl radical and the phospholyl anion. The main drawback of this synthesis is the formation of phenyl anion as a side product. This anion can interfere with the subsequent reactions of the phospholyl anion. In some instances, it can even react with the starting phosphole to yield another phospholyl anion. This is the case with 1,2,5-triphenylphosphole⁷⁸ (eq 34). Thus,



a lot of effort has been devoted to the solution of this problem. The classical technique using *tert*-butyl chloride to selectively destroy the phenyl anion appears not to be very reliable. Two other techniques have demonstrated their effectiveness. The first one involves a metathetical exchange of the alkali metal for another less electropositive metal (eq 35). The new phenyl-



metal derivative thus obtained has a reduced nucleophilicity. An additional advantage when using aluminum lies in the positive catalytic effect of AlCl₃ upon the subsequent alkylation of the phospholyl anion. Almost quantitative P-R bond formation is often achieved as illustrated by eq 36.⁸² The second tech-



nique replaces the cleavage of a P-Ph bond by the cleavage of a P-P or P-CH₂-CH₂-P bond. No side product is formed in that case (eq 37, 38). Full use of this technique is still to come. Table II lists all the phospholyl anions described in the literature up to now with some details on their syntheses.

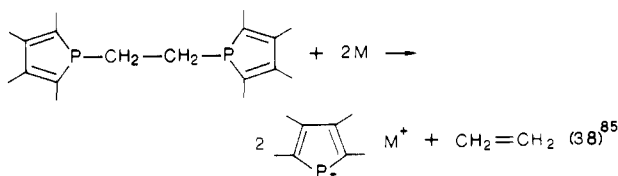
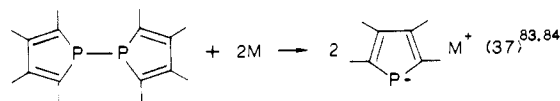
















TABLE II. Synthesis of Phospholyl Anions^a

phospholyl anion	cleaved bond	metal	main ref
	P-Ph	Li	4
	P-Ph	Li	25
	P-Ph	Li	25
	P-Ph	Li	4, 79
	P-Ph	Na-naphthalene	79
	P-CH ₂ -CH ₂ -P	Li	85
	P-Ph	K	39
	P-Ph	Li	4
	P-Ph	Li	40
	P-Ph	Li	40
	P-P	Li	83
	P-Ph	K	4, 39
	P-Ph	Li	39
	P-Ph	Na	36
	P-Ph	K	86
	P-Ph	K	86
	P-Ph	K	29
	P-Ph	Li	30
	P-P	Na-naphthalene	84
	P-P	Na-naphthalene	84

^a See eq 33, 37, and 38.

II. Physicochemical Data and Theoretical Problems

A. 1H-Phospholes

1. Structural Data

Some structural data concerning phospholes and their derivatives are collected in Table III. The phosphorus of trivalent phospholes is pyramidal ($\alpha + 2\delta \ll 360^\circ$). Nevertheless, the shortening of the intracyclic P-C bonds in **22** (1.783 Å versus ca. 1.84 Å for a normal P-C single bond) indicates that some kind of electronic delocalization is operative in the C-unsubstituted phosphole ring. The same kind of argument suggests that this delocalization is switched off by the 2,5-diphenyl substitution in **17**. Apparently, the 2-CO₂R substitution has the same effect. Indeed, the data for phosphole **25** and its *P*-sulfide **24** are closely similar. These observations clearly suggest that the electronic delocalization is weak in the phosphole ring since it is possible to switch it off easily. Two structural criteria for assessing

heteroaromaticity lead to the same conclusion. The crudest one relies on the (*c* - *b*) difference (see Table III). The smallest the difference, the highest the delocalization within the ring. The data are the following:⁷¹ pyrrole, 0.035 Å; thiophene, 0.053 Å; furan, 0.07 Å; phosphole **22**, 0.095 Å; cyclopentadiene, 0.127 Å, which gives the same order by decreasing aromaticity. The second more sophisticated criterion has been devised recently by Bird.⁹⁴ The order thus obtained is slightly different (thiophene > pyrrole >> furan > phosphole), but the overall conclusion remains the same: the phosphole ring is only weakly aromatic.

Before leaving the subject, it is interesting to note that trivalent phospholes are strained. The \angle CPC intracyclic bond angle is close to 90° in all cases (versus ca. 100° in acyclic phosphines). On the other hand, the phosphorane **26** is an almost perfect triangular bipyramid and the phosphole ring logically occupies a strain-free axial-equatorial position. The apical intracyclic P-C bond becomes very weak and this has interesting chemical consequences, which will be discussed later.

2. Spectroscopic Data

Almost all the papers dealing with phosphole chemistry contain NMR data concerning some derivatives of this ring. In many cases, these data have been recorded in order to establish whether or not this ring is aromatic. Today, this kind of debate is over, and the various arguments dealing with this problem and based upon NMR spectroscopy seem rather unconvincing. Since these NMR data have been collected and discussed in many older reviews (see especially ref 11, 13, and the book of Verkade and Quin mentioned in ref 16), the discussion will be focused here on the most recent and significant aspects of this topic.

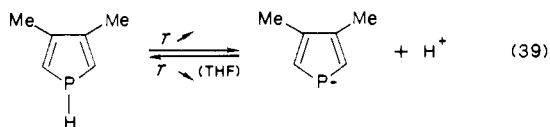
The recent characterization of the unstable P-unsubstituted phospholes at low temperatures⁴ has allowed a first series of ¹J(P-H) coupling constants to be recorded. The data are as follows: parent molecule (**3**), ¹J(P-H) = 234 Hz; 3,4-dimethylphosphole, ¹J(P-H) = 217 Hz; 2,5-diphenylphosphole, ¹J(P-H) = 232 Hz; 2,3,4,5-tetraphenylphosphole, ¹J(P-H) = 218 Hz. As it can be seen, these coupling constants are on the high side (the normal range for P^{III} compounds is between 155 and 235 Hz⁹⁵). According to Goetz et al.,⁹⁶ the ¹J(P-H) coupling constant shows a surprising indirect proportionality to the s character of the P-H bond. Thus, the results on phospholes would mean that the s character of the phosphole P-H bond is low and, conversely, the s character of the lone pair rather high. In turn, this would suggest a low delocalization within the ring. This conclusion is similar to that of Allen and Taylor,^{97,98} who have studied the ¹J(⁷⁷Se-³¹P) coupling constants in some phosphole selenides. These couplings are larger than for ordinary phosphine selenides, indicating that the s character of the phosphorus orbital involved in the bonding to selenium (i.e., the lone pair) is higher than usual. Another point of interest is the rather high sensitivity of the ¹J(P-H) couplings in **3** and analogues to the temperature. For 3,4-dimethylphosphole, this coupling varies between 224 and 216 Hz in THF when the temperature is raised from 173 to 323 K.⁴ Since no variation is observed in a non-ionizing

TABLE III. Structural Data for Phospholes^a

compound	no.	bond angles, deg		bond lengths, Å				ref
		α	δ (mean)	a (mean)	b (mean)	c	d	
	22	90.7	106	1.783	1.343	1.438	1.858	71, 87
	17		105.3	1.822	1.349	1.440	1.822	88
	23	93.3	108.1	1.810	1.355	1.505	1.796	89
	24	91.4	108.1	1.813, 1.786	1.353, 1.336	1.494	1.807	90
	25	89.2	102.9	1.804, 1.789	1.360, 1.332	1.472	1.840	91
	26	87.9		1.837, 1.885	1.337	1.462		92
	27	91.8		1.785	1.374	1.442		93

^aMetal complexes are excluded. The corresponding data are collected in ref 15.

solvent such as toluene, the variation in THF is ascribed to the ionization of the P-H bond⁴ (eq 39).







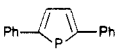
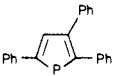
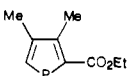
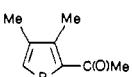
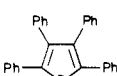
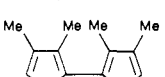
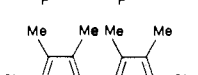


Three papers specifically deal with the ¹³C NMR spectra of phospholes.⁹⁹⁻¹⁰¹ In fact, no clear-cut conclusions can be drawn from these data concerning the aromaticity of the ring. A general leveling of the chemical shifts of the ring carbons is noted as more or less expected for an aromatic system, but the intracyclic ¹J(C-P) coupling constants are very low (ca. 5 Hz), contrary to what would be expected for a bond order greater than 1. Considering now the ³¹P NMR data, it can be stated as a general rule that the phosphorus of a phosphole resonates at lower field than the phosphorus of the corresponding 2- and 3-phospholenes ($\Delta\delta = \text{ca. } +10$ and $+30$ ppm, respectively), but it is impossible to discriminate between the various electronic

and geometrical factors involved in this deshielding. Some representative data concerning trivalent phospholes are collected in Table IV.

Various other spectroscopic data on phospholes are scattered throughout the literature. They concern dipole moments,¹⁰³ photoelectron spectra,^{104,105} and UV spectra.^{24,32,34,41,42,106,106a} As a general statement, they can be considered as more in favor of a nonaromatic phosphole ring. Indeed, the dipole moments are directed from the ring to the heteroatom (negative end), contrary to what occurs in pyrroles, suggesting a higher localization of the lone pair on the heteroatom in the first case. Similarly, the energy of the phosphorus lone pair orbital appears to be virtually unchanged when comparing a phospholane and a phosphole according to the results of photoelectron spectroscopic studies. Even though Epiotis¹⁰⁷ has shown later that this observation is not strictly incompatible with an aromatic phosphole ring, it can be nevertheless stated that it is more in favor of a nonaromatic system. Finally, methyl substitution of the ring causes a blue shift in the UV spectrum¹⁰⁶ contrary to what happens with aromatic heterocycles.

TABLE IV. ^{31}P NMR Data of Some Monocyclic Tervalent Phospholes^a

nucleus	P-substituent							
	H	Me	<i>n</i> -Bu	<i>t</i> -Bu	CH ₂ Ph	Ph	P-P	OMe
	-49.2 [4]	-8.7	+5.5		+8	+7.8		
		-7.3				+14.2 [25]		
		-6.9	+8.5	+40.5	+11.5	+9.5		
		+3						
	-59.4 [4]	-20.2	-6.5	+27.5	-3	-2.5	-25.3 [102]	
		-12.6						
	-54.2 [4]	-15.5 [78]				+3	-27.9 [78]	+112.9 [78]
		+0.5 [83]					-11.8 [83]	
				+34.3		+5		
			+6.8	+35.1		+5		
	-40.9 [4]					+13.9 [69]		
						+12.5 [30]		
							-11.6 [84]	

^a Data collected in ref 11 except when otherwise noted; chemical shifts were recorded either in CDCl₃ or for the neat products; downfield shifts are noted positive from external 85% H₃PO₄.

3. The Aromaticity Problem

The problem of phosphole aromaticity has been a highly controversial matter for a while, but now a general agreement has been reached. As seen in the two preceding sections, structural and spectroscopic data are in favor of a low aromaticity within the phosphole ring. The structural data are of course more reliable than the spectroscopic ones. Similarly, the chemical properties of the phospholes are more compatible with a weakly aromatic system as it will be seen later. For example, protonation occurs at the heteroatom in phospholes (see Section III.A.1) whereas it occurs at the α -carbons in pyrroles. Of course, numerous theoretical calculations have been performed on the phosphole ring in order to investigate this aromaticity problem.^{105,108-115a} But only one (performed by Palmer^{111,114}) uses both an elaborate ab initio formalism and the correct experimental geometry. Its conclusions seem to be quite clear. The estimated resonance energies are -149 kJ/mol for pyrrole, -124 kJ/mol for thiophene, -89 kJ/mol for furan, and -54 kJ/mol for phosphole in its pyramidal

ground state. On another side, Mislow has obtained important results concerning the pyramidal inversion barrier of phosphorus.^{40,116} This barrier is abnormally low in phospholes, ca. 16 kcal/mol versus ca. 36 kcal/mol in a "normal" cyclic phosphine such as phospholane. This 20 kcal/mol lowering is ascribed by Mislow to the aromatic stabilization of the planar transition state of phospholes. Indeed, in the planar state, the $n\pi$ overlap between the lone pair and the π dienic system is at its maximum whereas it sharply decreases when phosphorus becomes pyramidal. Phospholes are non-planar just because the aromatic stabilization of the planar state is insufficient to overcome the very high inversion barrier of phosphorus. The situation is the reverse in pyrroles as a consequence of the low pyramidal inversion barrier of nitrogen. At this point, it must be noted that no reliable calculations exist on the planar state of phospholes (a careful optimization of the geometry is necessary). Before leaving the subject, two theoretical works concerning spiropospholium salts¹¹⁷ and phosphole-substituted silicium ions¹¹⁸ must be mentioned.

TABLE V. ^{31}P NMR Data of Phospholyl Anions^a

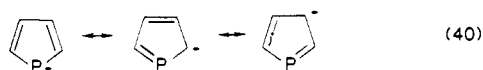
phospholyl anion	solvent	counterion	side product	chemical shift	ref
	THF	Li ⁺	PhLi	+76.6	4
	THF	Li ⁺	none	+59.03	85
	THF	Li ⁺	PhLi	+58.9	4
	THF	Li ⁺	PhLi	+78.7	4
	THF	Li ⁺	PhLi	+102.5	78
	THF	K ⁺	Ph(CH ₂) ₄ OK?	+97	119
	THF	K ⁺	Ph(CH ₂) ₄ OK?	+98.8	4
	THF	K ⁺	Ph(CH ₂) ₄ OK?	+73.3	86
	THF	K ⁺	Ph(CH ₂) ₄ OK?	+81.7	86
	THF	K ⁺	Ph(CH ₂) ₄ OK?	+81.7	86
	THF	Li ⁺	PhLi	+56.7	30

^a δ positive for downfield shifts from external 85% H₃PO₄.

B. Phospholyl Anions

NMR Data and Theoretical Calculations

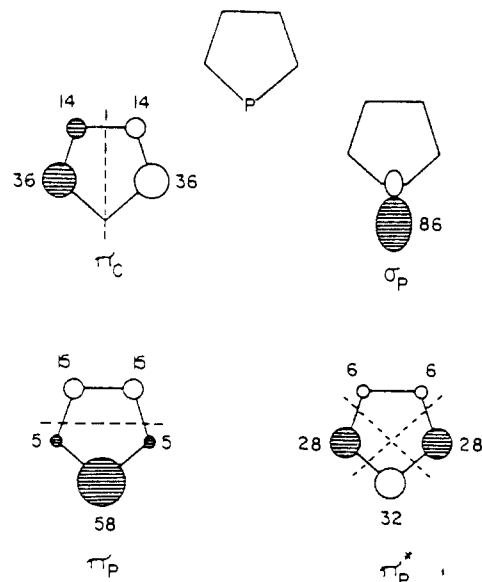
Contrary to classical phosphide anions R₂P⁻ whose phosphorus resonates around 0 ppm (versus H₃PO₄), the phospholyl anions resonate at much lower fields as first noted by Quin.⁸⁶ The available data are collected in Table V. The chemical shifts show only a low sensitivity to the nature of the counterion and this fact suggests that the P-M bond is highly ionized. The ^{31}P deshielding has been correlated by Quin⁸⁶ with the delocalization of the negative charge all over the ring, which gives some phosphalkene character to these species (eq 40). The availability of pure 3,4-di-



methylphospholyl anion first obtained by the technique depicted in eq 38⁸⁵ has also recently allowed the study of this type of species by ^1H and ^{13}C NMR spectroscopy. When the ^{13}C NMR spectra of 1-phenyl-3,4-dimethylphosphole (15)¹⁰¹ and the corresponding anion are compared,⁸⁵ it appears that the $^1J(\text{C}-\text{P})$ coupling constant within the ring sharply increases from 7.3 Hz in 15 to 45 Hz in the anion. This increase can be correlated with the double-bond character of the P-C bond in the anion since such high values are characteristic of phosphalkenes.¹²⁰

The first theoretical calculations on phospholyl anion were performed by Kaufmann¹¹³ using the classical CNDO/2 formalism. The geometry was obtained by just flattening the nonplanar 1-benzylphosphole.⁷¹ It included rather long P-C bonds and inequivalent C=C bond lengths. Recently, Pfister-Guillouzo¹²¹ and Fenske¹²² published more reliable data based on geometries that were deduced from the structures of η^5 -phospholyl-manganese and -iron complexes with rather

SCHEME I. Significant Orbitals of the Phospholyl Anions (Reprinted with Permission from ref 122. Copyright 1983 American Chemical Society)



^a Orbital ordering: $\pi_c < \sigma_p < \pi_p(\text{HOMO}) \ll \pi_p^*(\text{LUMO})$.

short P-C and equivalent C=C bonds. More sophisticated ab initio formalisms were used. In the three cases, however, the main conclusion was identical: the phospholyl anion is highly aromatic as is the isoelectronic thiophene. Since, according to these calculations, the net negative charge at phosphorus is rather high and the HOMO is mainly localized at phosphorus, both the electrophilic attacks under charge and frontier orbital controls are predicted to take place at phosphorus as experimentally observed. Scheme I depicts the most significant orbitals of the phospholyl anion as calculated by Fenske.¹²² The three occupied orbitals π_c , σ_p , and π_p are so close in energy that inversion of the π_c and π_p

orbitals has been observed when EHT and STO-3G data are compared.¹²¹

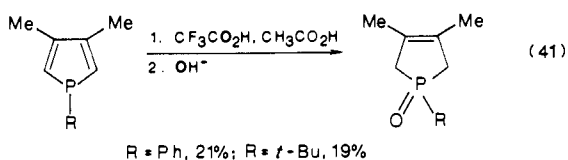
Before leaving this subject, it is interesting to note that a preliminary theoretical study of the phospholyl cation has been performed by Russian authors.¹²³ This antiaromatic cation is predicted to be folded around the C α -C α' axis (dihedral angle ca. 17°) and to have very inequivalent C=C bond lengths (1.512 and 1.346 Å, respectively).

III. Chemical Properties

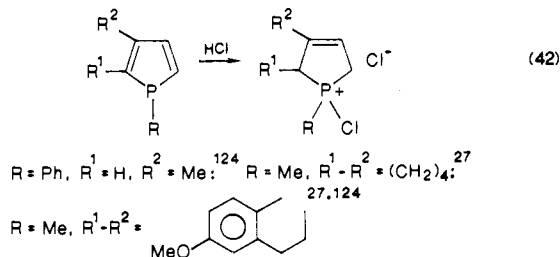
A. 1H-Phospholes

1. Nucleophilic Properties of Phosphorus

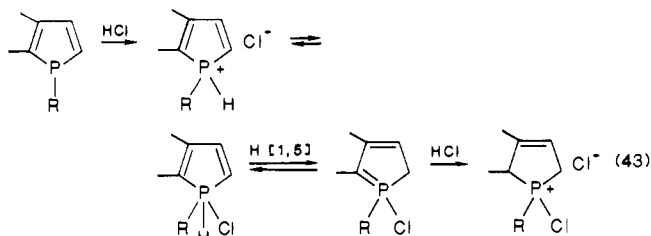
The reaction of phospholes with acids was understood only very recently.¹²⁴ It leads to phospholene derivatives that formally result from the protonation of the phosphole ring at carbon. Two such reactions have been described. In the first one, a phospholene oxide is obtained¹²⁵ (eq 41).



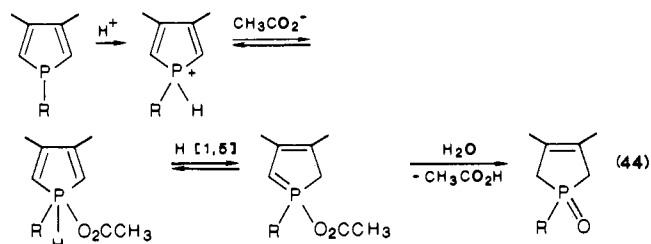
The second reaction^{27,124} is just the reverse of the synthesis of phospholes by dehydrohalogenation of the McCormack cycloadducts (see eq 1). It was initially taken as proof of the C-protonation of phospholes by HCl²⁷ (eq 42).



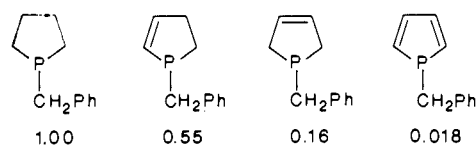
Closer inspection by ³¹P NMR spectroscopy of the reaction of phospholes with dry HCl in CD₂Cl₂ at -90 °C conclusively showed that the initial protonation site of the cycle was in fact phosphorus,¹²⁴ in complete agreement with the various physicochemical studies that suggest only a weak delocalization of the phosphorus lone pair all over the ring (see Section II.A.3). When the temperature is raised, the counterion Cl⁻ attacks the positive phosphorus, leading to a phosphorane in which a H [1,5] sigmatropic shift easily takes place as already discussed in Section I.B. Addition of HCl onto the P=C bond of the cyclic ylide thus formed then gives the observed products (eq 43). If the rather



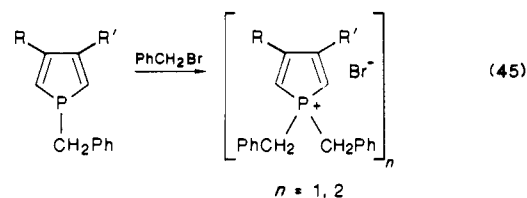
nucleophilic Cl⁻ is replaced by bulky counterions with low nucleophilicity, this hydrogen shift is either slowed down (CF₃SO₃⁻¹²⁴) or completely stopped (TaCl₆^{-126,127}). Stable 1,2,5-triphenylphospholium salts have thus been obtained,^{35,126,127} showing a characteristic ¹J(P-H) coupling (ca. 502 Hz³⁵) and a typical P-H stretching frequency (ν (P-H) = 2410 cm⁻¹^{126,127}). The mechanism of the formal hydration depicted in eq 41 is very probably quite similar (eq 44). Thus, contrary to pyrroles that



are protonated at carbons,^{128,129} phospholes behave like normal phosphines and are protonated at the heteroatom. The only consequence of the weak cyclic delocalization of the lone pair is their reduced basicity: the pK_a of 1-methylphosphole is only 0.5⁴¹ versus more than 5 for acyclic divinylphosphines. This reduced nucleophilicity of the phosphole lone pair is also observed in the quaternization reactions. The following relative quaternization rates by PhCH₂Br in Me₂CO are illustrative:¹³⁰

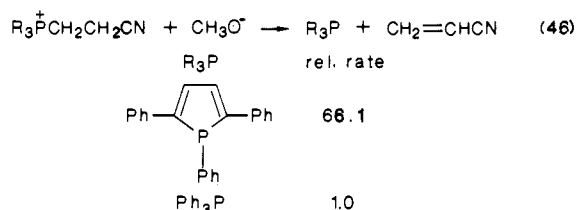


The quaternization rates are also very sensitive to the substitution pattern of the ring¹³⁰ (eq 45).



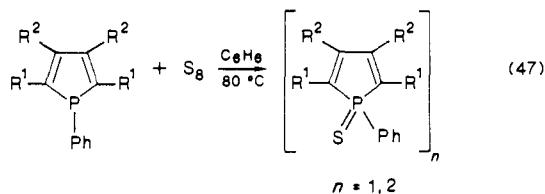
R = R' = H, 11 days, 28%; R = H, R' = Me, 2 days, 83%;
R = R' = Me, 2 days, 100%

The low quaternization rates of phospholes are paralleled by the high dequaternization rates of their (β -cyanoethyl)phospholium salts¹³¹ (eq 46).



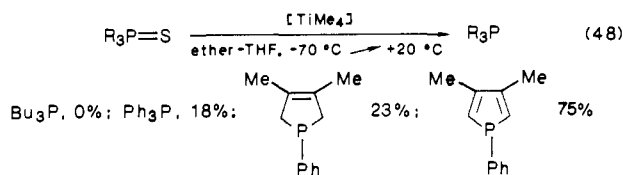
Much less data are available on the oxidation of phospholes. This oxidation is best carried out with H₂O₂ in organic medium at low temperatures. Most of the phosphole oxides thus obtained undergo rapid dimerization (see Section III.A.4). Millar¹³² has shown that the dissociation energy of the P=O bond is lower in pentaphenylphosphole oxide (ca. 100 kcal/mol) than in a normal phosphine oxide such as Ph₃PO (ca. 128

kcal/mol). The same kind of effect is also found with phosphole sulfides. The sulfurization rates are very sensitive to the substitution pattern of the phosphole ring¹³³ as the quaternization rates (eq 47). Besides, as

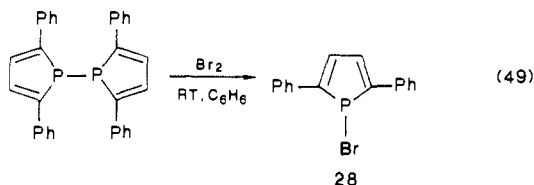


$\text{R}^1 = \text{R}^2 = \text{Ph}$, 48 h, 50%; $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{H}$; 6 h, 35%; $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Me}$, 3 h, 90%

expected, monomeric phosphole sulfides are easier to reduce than ordinary phosphine sulfides¹³⁴ (eq 48). Phospholes also react with selenium although rather sluggishly. A limited number of phosphole selenides have thus been obtained.^{34,44,97,98,125}



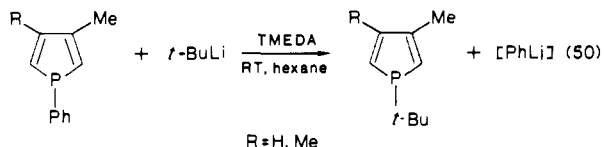
The reaction of phospholes with halogens has never been seriously investigated. Apparently, it does not give tractable products, although, in one instance, 1-bromophosphole **28** has been made via the cleavage of a P-P bond by bromine⁷⁸ (eq 49).



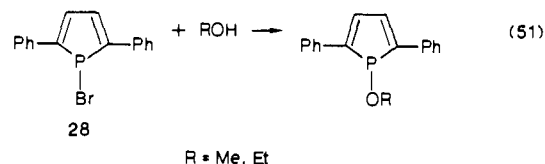
Finally, Russian authors have described the reaction of pentaphenylphosphole with various nitrile imines in which the phosphorus lone pair is also involved as a nucleophile.¹³⁵ Phospholium salts are thus obtained.

2. Electrophilic Properties of Phosphorus

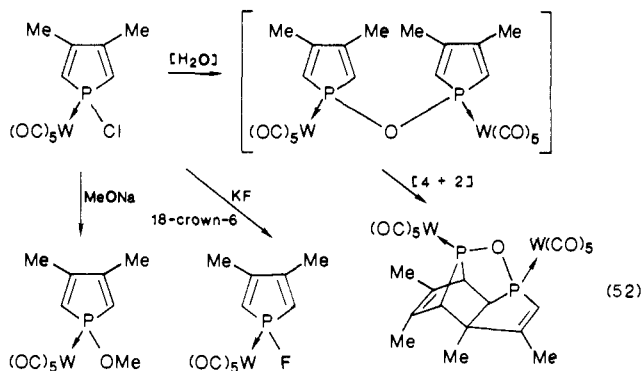
A priori, the partial delocalization of the phosphole lone pair will enhance the electrophilicity of phosphorus. No quantitative data are available. However, in some instances, clean nucleophilic attacks at phosphorus have been observed. For example, 1-phenylphospholes easily react with *tert*-butyllithium; 1-*tert*-butylphospholes have thus been obtained for the first time^{21,125} (eq 50). Similar reactions have been studied



with more classical phosphines.¹³⁶ They generally yield complicated mixtures of products, and their mechanism is still controversial. In the same vein, 1-bromo-2,5-diphenylphosphole (**28**) has been shown to react with alcohols in the normal way to yield the first two known 1-alkoxyphospholes⁷⁸ (eq 51). Compound **28** also cleanly reacts with cyclopentadienyllithium to give a

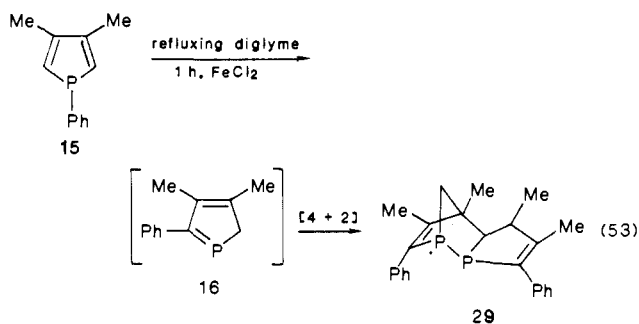


mixture of isomeric 1-cyclopentadienyl-2,5-diphenylphospholes.¹³⁷ On the other hand, the reaction of 1-chloro-2,3,4,5-tetraphenylphosphole with some organometallic anions has been investigated by Abel.¹³⁸ Finally, when stabilized by complexation with pentacarbonyltungsten, 1-chloro-3,4-dimethylphosphole shows a normal reactivity toward MeO^- , H_2O , and F^- ¹³⁹ (eq 52).

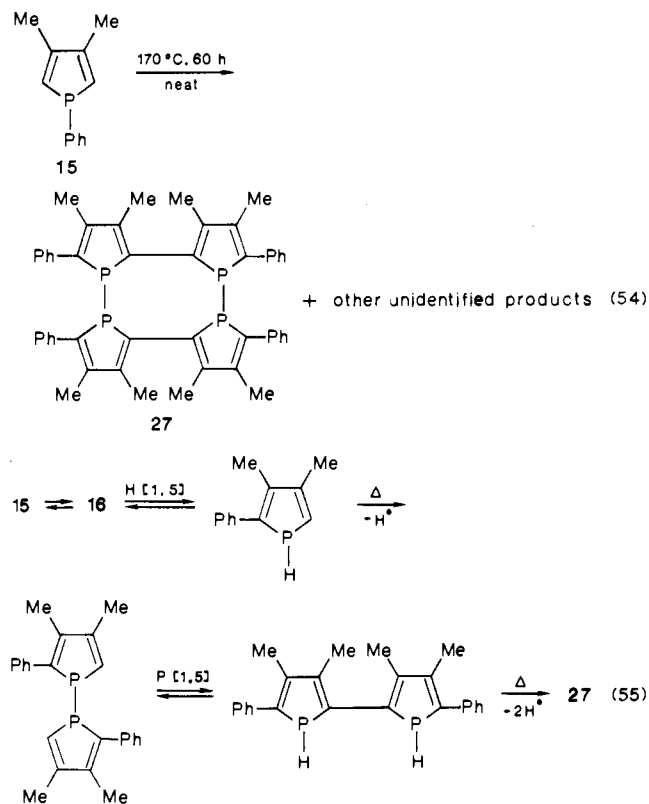


3. Heat- and UV-Induced Transformations

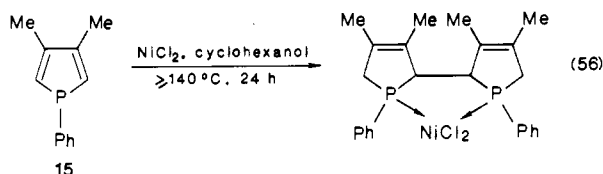
As a general statement, it can be said that the substitution pattern of the phosphole ring has a profound impact upon its behavior toward heat and UV irradiation. Presently, only two phospholes have been seriously investigated from this standpoint, namely 1-phenyl-3,4-dimethylphosphole (**15**) and 1,2,5-triphenylphosphole (**17**). Phosphole **15** appears to be insensitive toward a prolonged irradiation by a 250-W medium-pressure mercury lamp. Only some decomposition is observed. On the contrary, this phosphole shows a rich and versatile behavior toward heat. When heated in the presence of catalytic amounts of FeCl_2 at ca. 150°C for 1 h, **15** gives the *2H*-phosphole dimer **29**¹⁴⁰ (eq 53). The phenyl [1,5] shift has already been dis-



cussed in Section I.B. The *2H*-phosphole **16** thus produced instantly undergoes a [4 + 2] Diels-Alder dimerization leading to **29**. If now phosphole **15** is heated for a prolonged period of time at ca. 170°C , the transformation proceeds further and yields inter alia the red tetramer **27**⁸⁴ (eq 54). This tetramer crystallizes out from the reaction mixture and is thus easily recovered. The mechanism of its formation is obscure but almost certainly involves the transient *2H*-phosphole **16**. A tentative scheme is depicted in eq 55. Still

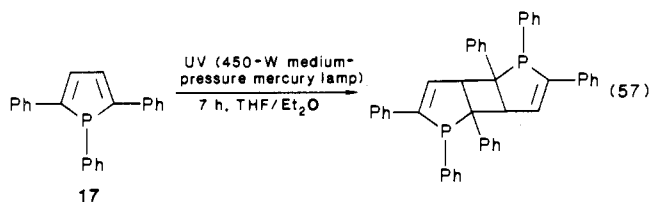


another behavior of 15 is observed in the presence of stoichiometric amounts of nickel chloride. With an alcohol as the reaction medium, a reductive dimerization takes place^{141,142} (eq 56). The source of hydrogen

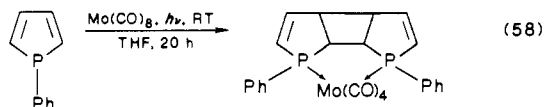


is the hydroxy group of the solvent as demonstrated by deuterium-labeling experiments. The biphospholene thus produced can be recovered from its nickel complex through decomplexation by sodium cyanide. The mechanism of this reaction is presently unknown.

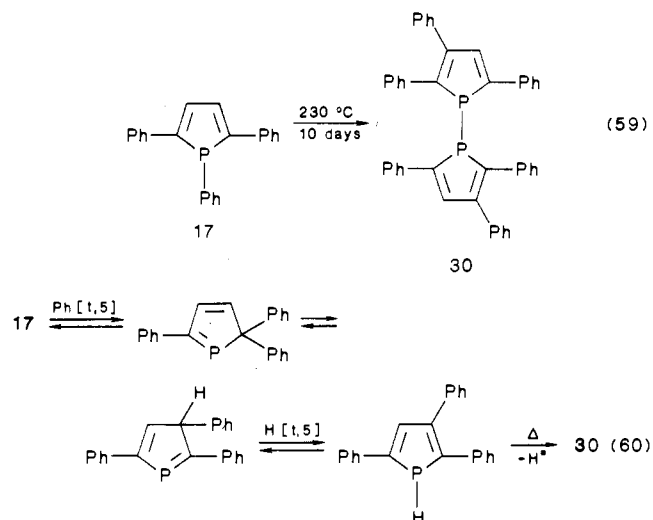
The behavior of 17 is entirely different. Under UV irradiation, it does give a classical [2 + 2] "head to tail" dimer¹⁴³ (eq 57).



This sensitivity of 17 toward UV irradiation probably reflects the weaker aromatic stabilization of 17 when compared to 15. This point has already been discussed elsewhere.¹³ A similar [2 + 2] "head to head" dimerization of 1-phenylphosphole has been observed in the coordination sphere of molybdenum¹⁴⁴ (eq 58). The

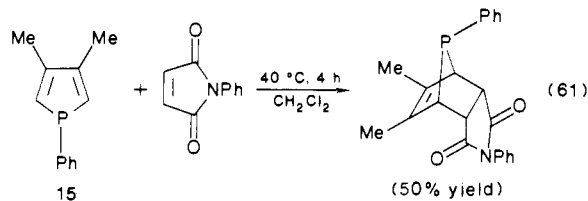


behavior of 17 toward heat is again different from that of 15. Upon prolonged heating, a 1,1'-biphospholyl is obtained⁸³ (eq 59). The most likely mechanism of this transformation is depicted in eq 60. The similarity with the mechanism depicted in eq 55 is obvious.

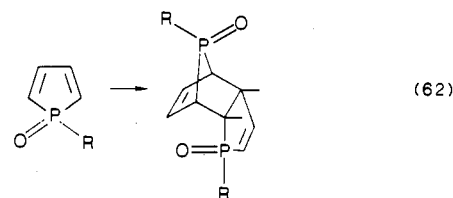


4. Diels-Alder Reactivity of the Dienic System

As a general rule, it can be stated that the dienic system of trivalent phospholes is poorly reactive. This is obviously correlated with the cyclic delocalization within the ring, which, in spite of its relative weakness, reduces the availability of the four π -electrons. Nevertheless in some instances, it has been possible to force trivalent phospholes to undergo Diels-Alder reactions. For example, it has been stated^{34,44} that both 1,2,5-triphenyl- and 1,2,3,4,5-pentaphenylphospholes sluggishly react with maleic anhydride at high temperatures (110–150 °C). Low yields (3–11%) and poor characterization of the products cast some doubt upon these rather old data. More convincing is the recent discovery that 15 cleanly reacts with *N*-phenylmaleimide at moderate temperature to give a good yield of the expected [4 + 2] adduct¹⁴⁵ (eq 61).

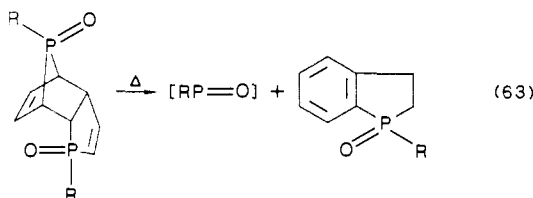


Upon oxidation, sulfurization, quaternization, or complexation of the phosphole lone pair, the reactivity of the dienic system sharply increases as expected. Phosphole oxides are so reactive that they normally instantly dimerize to give the [4 + 2] endo dimers^{21,23,42,125,146} (eq 62).

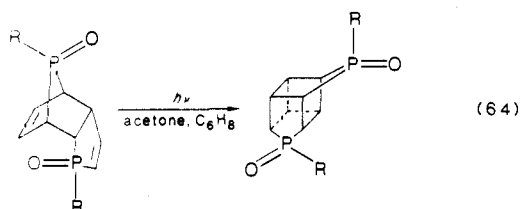


As a general rule, only pentasubstituted phosphole oxides are stable as monomers.^{29,43,44,49} Among the no-

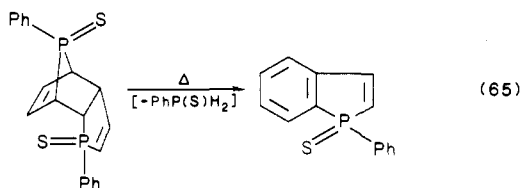
table exceptions to this statement is 1,2,5-triphenylphosphole oxide,³⁴ the dienic system of which is probably partly stabilized by conjugation with the 2,5-diphenyl substituents. The geometry of one such dimer has been established by X-ray crystal structure analysis¹⁴⁷ (see also ref 152). The phosphorus at the bridge appears to be highly strained (intracyclic CPC angle $\approx 87^\circ$). This strain imparts several interesting properties to this phosphorus atom. It favors the formation of transient pentacoordinate trigonal-bipyramidal structures. This explains why the P(O)OEt at the bridge of such a dimer is hydrolyzed 4×10^4 times faster than in the corresponding monocyclic phosphol-3-ene.¹⁴⁸ This strain also explains why it is possible to insert oxygen within one of the P-C bonds of such bridges (P-C \rightarrow P-O-C) by using peracids.¹⁴⁹⁻¹⁵² The easy splitting of the bridge has been used as a route to the dihydrophosphindole system¹⁵³ (eq 63). Such a split-



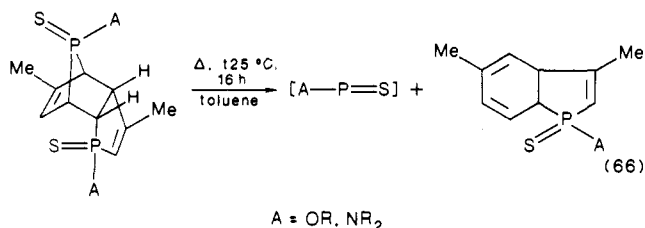
ting also readily takes place during the deoxygenation of these dimeric oxides. Only reducing agents (e.g., HSiCl_3 - $\text{C}_5\text{H}_5\text{N}$) that avoid the transient formation of a phosphorane can effect the reduction without loss of phosphorus.¹⁵⁴⁻¹⁵⁶ Finally, another chemical property related to the endo geometry of these dimers deserves to be noted. Upon UV irradiation, they give an interesting cage structure^{157,158} (eq 64).



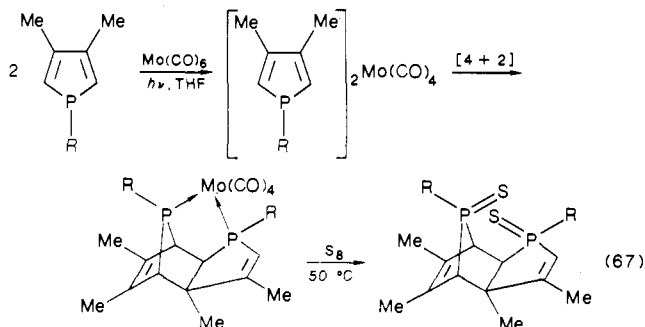
The tendency to dimerize is weaker for phosphole sulfides than for phosphole oxides. For example, 3,4-dimethylphosphole sulfides are normally monomeric²¹ whereas the corresponding oxides are dimeric. The general properties of the dimeric sulfides closely parallel those of the dimeric oxides. The bridge easily collapses and this has been used in two ways. First, this splitting provides an access to the phosphindole system¹⁵⁹ (eq 65). It is interesting to note that the presence of sulfur



induces the dehydrogenation of the primary decomposition product contrary to what happens in the P=O series (see eq 63). The same basic scheme can be used to generate phosphinidene sulfides. A first example is depicted in eq 66.¹⁶⁰ Quite interestingly, it is possible to change the endo geometry at the junction by performing the [4 + 2] dimerization within the coordina-



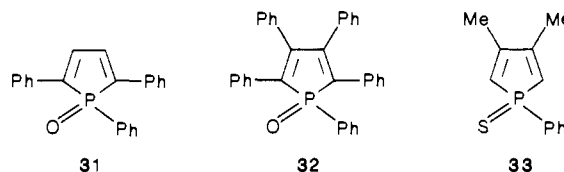
tion sphere of a metal¹⁴¹ (eq 67). The exo dimeric



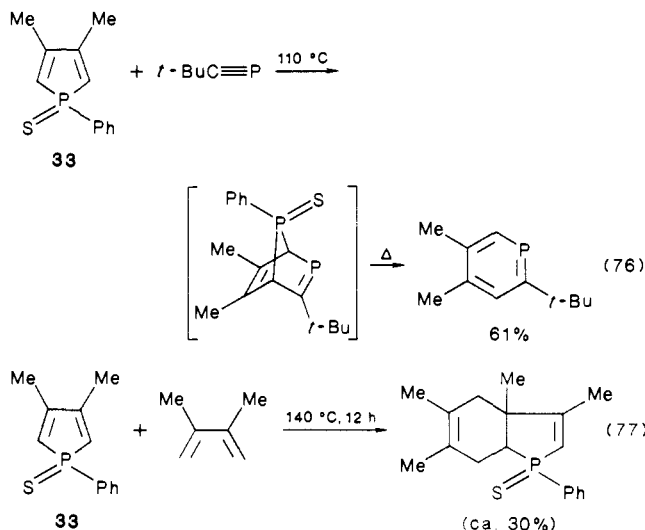
phosphole sulfides thus obtained are much more strained at the bridge than the corresponding endo dimers (CPC angle ca. 80° versus ca. 87°). As a consequence, they can be used as much more efficient precursors of phosphinidene sulfides than their endo counterparts.¹⁴⁴ The change of geometry also induces sharp changes in the $^3J(\text{P-P})$ coupling constants. These are close to 0 Hz in the exo and close to 45 Hz in the endo dimers.¹⁴⁴

As a general rule, the behaviors of phospholium salts and phosphole sulfides are closely parallel. This means that the main factor controlling the dimerization of phospholium salts is the substitution pattern of the dienic system. Nevertheless, in some instances, the bulkiness of the substituents at phosphorus plays some role too. For example, 1,1,3-trimethylphospholium iodide dimerizes whereas 1,1-dibenzyl-3-methylphospholium bromide is stable as a monomer.¹⁶¹ In the second case, the bulky benzyl groups hinder the dienic system and prevent the [4 + 2] cycloaddition. Only the spectral properties of dimeric phospholium salts have been studied in some depth so far.^{158,158a}

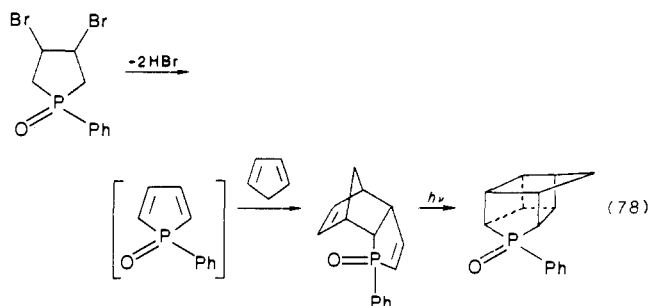
The study of the reactivity of the phosphole dienic system toward external dienes or dienophiles is obviously hampered by the tendency of phosphole derivatives to dimerize. The bulk of the work has been done with stable monomeric derivatives such as 1,2,5-triphenylphosphole oxide (31), 1,2,3,4,5-pentaphenylphosphole oxide (32), 1-phenyl-3,4-dimethylphosphole sulfide (33), and several P complexes. In most cases,



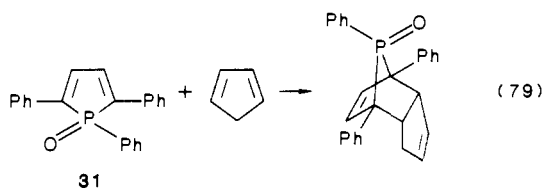
the phosphole derivative acts as the 4π component of the cycloaddition. With maleic anhydride and *N*-phenyl- or *N*-methylmaleimide, the reaction gives the normal [4 + 2] endo adducts^{34,44,145,151,152,162-164} (eq 68). Similarly, the reaction of sulfide 33 with 4-methyl-1,2,4-triazoline-3,5-dione gives the expected [4 + 2] adduct but as a mixture of two epimers.¹⁶³ These ad-



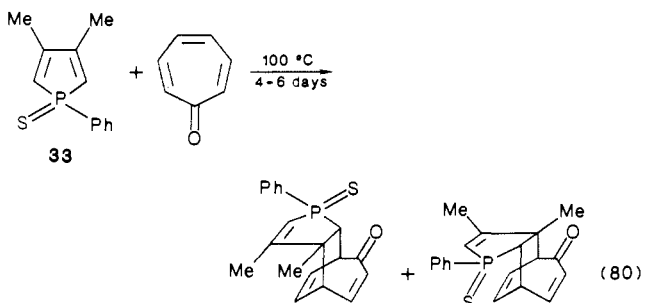
very interesting in this respect. It acts either as a diene or as a dienophile toward the phosphole system. For example, the transient monomeric 1-phenylphosphole oxide generated in situ by dehydrobromination of 3,4-dibromo-1-phenylphospholane oxide gives the [2 + 4] adduct¹⁷⁷ (eq 78). This adduct gives an interesting cage compound under UV irradiation. A similar behavior



had been noted earlier between 1-ethoxyphosphole oxide and cyclopentadiene.¹⁴⁶ On the contrary, the stable phosphole oxide 31 behaves as the 4π component toward cyclopentadiene¹⁷⁷ (eq 79). There is no obvious rationalization of these discrepancies.

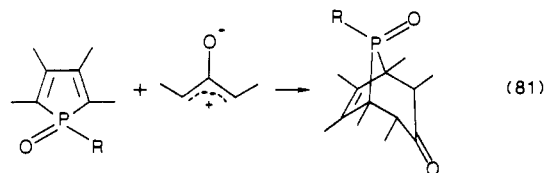


A last example of a phosphole derivative acting as a dienophile has been reported by Kashman.¹⁷⁸ Phosphole sulfide 33 and tropone react to give a mixture of isomeric [2 + 4] adducts (eq 80). No [4 + 6] cyclo-



addition is observed. Finally, the same group has de-

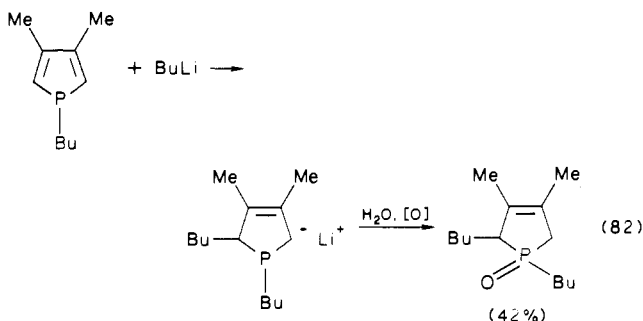
scribed the only known [4 + 3] cycloaddition involving the phosphole ring and a series of oxyallyl cations¹⁷⁹ (eq 81).



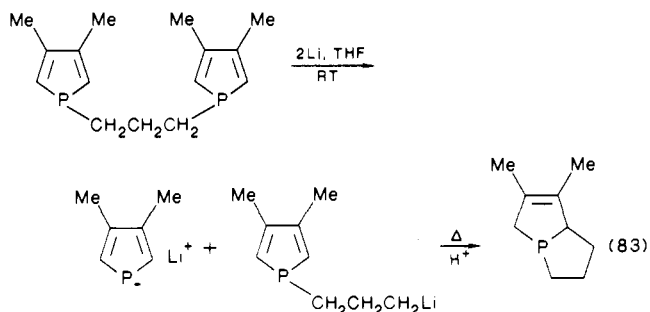
5. Other Reactions of the Dienic System

When the Diels–Alder cycloadditions are excluded, the two main classes of reactions taking place at the dienic system that have been investigated with phospholes (as with pyrroles, furans, and thiophenes) have been the reactions with alkyllithiums and the reactions under Friedel–Crafts conditions. Here again, sharp differences appear when the behavior of phospholes is compared with those of its nitrogen, oxygen, and sulfur analogues.

For example, metalation at the ring carbons is not observed when a phosphole is allowed to react with an alkyllithium²¹ (eq 82). This addition can compete with

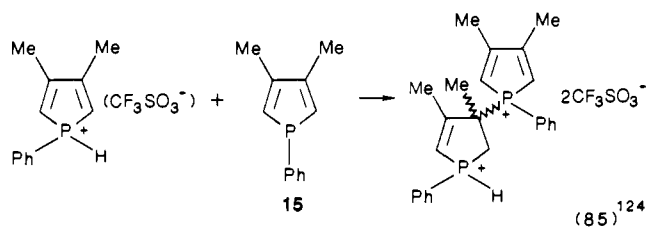
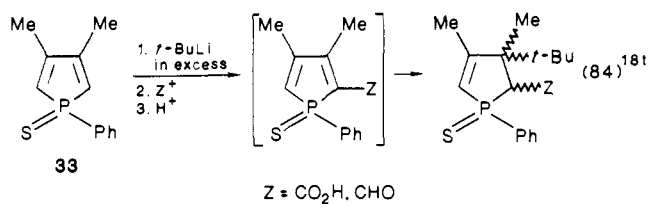


the substituent exchange described in eq 50. Recently, an interesting intramolecular version of this reaction has been discovered; it yields a new bicyclic system⁸⁵ (eq 83). At this point, it is clear that the behavior of

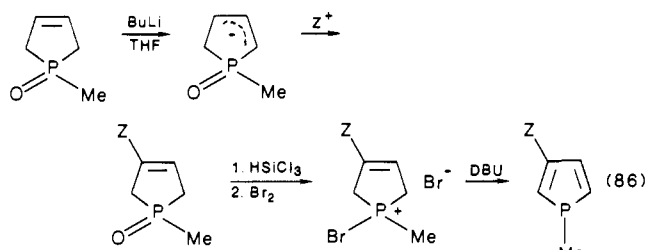


phospholes toward alkyllithiums again illustrates their weak aromaticity. In fact, this kind of nucleophilic addition onto phosphorus-activated $\text{C}=\text{C}$ double bonds had been observed earlier with vinylphosphines.¹⁸⁰ Nucleophilic attacks at the dienic system are, as expected, favored when phospholes are either oxidized, quaternized, or activated by electron-withdrawing groups. The two examples depicted in eq 84 and 85 are illustrative. In the second case, the nucleophile is not an alkyllithium any more but a phosphole lone pair.

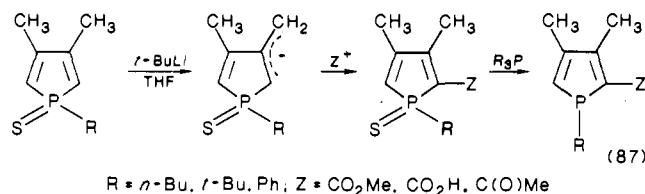
The behavior of phospholes in the presence of Lewis acids is also entirely different from those of pyrroles, furans, and thiophenes. Since the phosphorus lone pair retains a rather high Lewis basicity (see Section III.A.1),



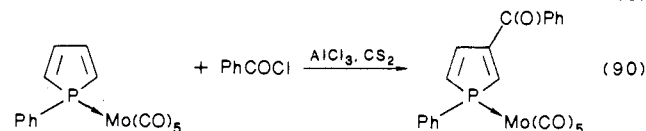
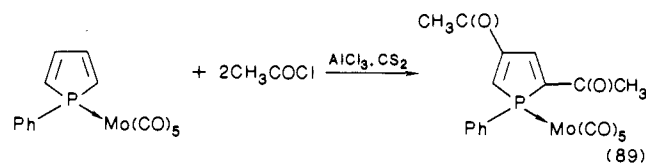
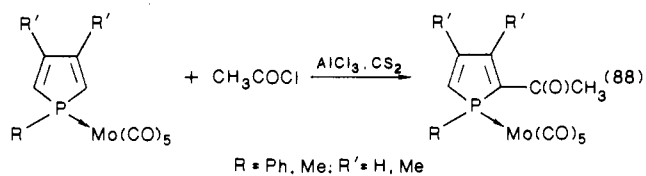
the Lewis acid tends to attack the phosphole ring at phosphorus and not at the diene. For a while, this precluded any kind of electrophilic functionalization of the phosphole ring. For that reason, the first two known routes to functional phospholes relied on rather tricky techniques. The first route was devised by Quin.^{24,26} The function is, in fact, installed on a phospholene ring via a classical P=O-promoted metalation (eq 86). The last step of this scheme relies on the



well-established phosphole synthesis from McCormack cycloadducts (eq 1). The overall yield is, of course, quite low and the generality is limited by the sensitivity of Z toward the various reagents used in this route. Besides, useless 2-phospholenes often appear as byproducts. The second route was devised by Mathey.¹⁸¹⁻¹⁸³ It relies on the abstraction of a methyl proton from a 3,4-dimethyl-substituted phosphole sulfide by *tert*-butyllithium (eq 87). Here, the generality is limited by

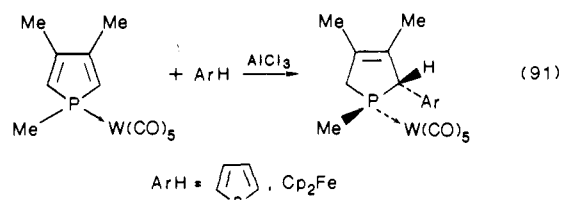


the necessary 3,4-dimethyl substitution, but the overall yields are higher. However, the genuine breakthrough came when it was found that it was possible to acylate the phosphole ring at carbon under Friedel-Crafts conditions provided that the phosphorus lone pair was blocked by complexation with pentacarbonylmolybdenum.¹⁸⁴ Equations 88-90 are representative. These acylations are very sensitive to steric hindrance. The benzylation described in eq 90 takes place at the β -position probably for this reason. Pentacarbonylmolybdenum is used for the protection of the phosphole lone pair because it does not deactivate the dienic system (electron donation through Mo→P π -back-bonding compensates electron withdrawal through P→Mo σ -bonding) and because it is fairly resistant toward



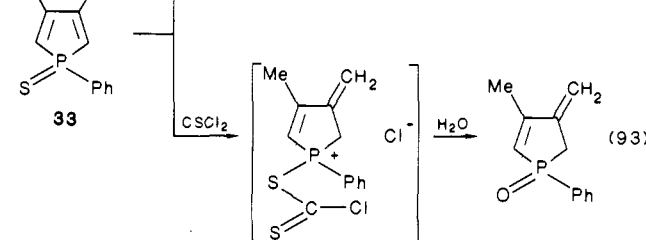
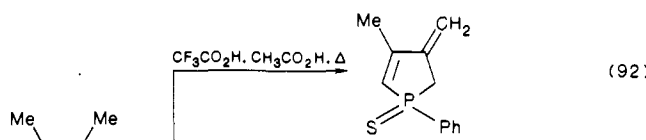
AlCl₃. The functional phospholes are recovered from their complexes through ligand exchange with CO or P(OMe)₃. Unfortunately, this scheme cannot be generalized to Vilsmeier formylation, thus indicating that the phosphole dienic system remains relatively unreactive toward electrophilic substitutions.

The phosphole dienic system can serve to alkylate an arene in the presence of AlCl₃ provided again that the phosphorus lone pair is blocked by complexation¹⁸⁷ (eq 91). A good stereochemical control of the ring arylation



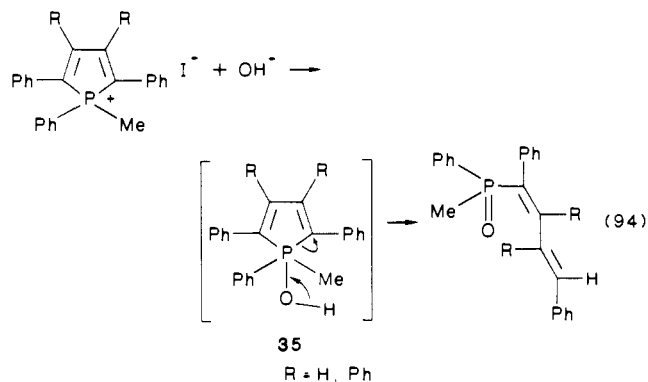
is observed. It seems logical to admit that AlCl₃ selectively attacks the side of the diene that is opposite to W(CO)₅ for steric reasons, thus leaving the other side free for the subsequent arylation.

Finally, it must be mentioned that the hydrogenation of phosphole oxide 31 into 1,2,5-triphenylphospholane oxide has been successfully carried out in the presence of hydrated platinum oxide³⁴ and that double-bond migrations have been observed on phosphole sulfide 33 as depicted in eq 92-93.^{125,163}

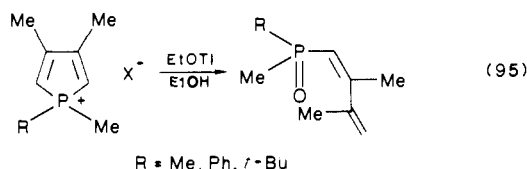


6. Ring Opening

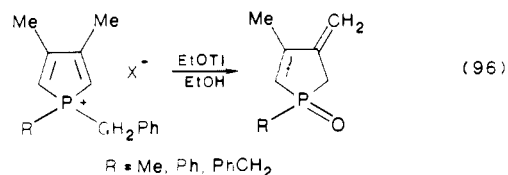
The only well-studied case of phosphole ring opening has been discovered by Bergesen¹⁸⁵ (eq 94). This reaction obeys a second-order kinetics (first-order dependence on the concentrations of OH⁻ and phosphonium ions). Its activation energy is very low (11-12



kcal/mol). The formation of the transient hydroxyphosphorane **35** is obviously favored by the cyclic strain of the phosphole ring (intracyclic CPC angle close to 90° ; see Table III). In **35**, which is assumed to have the classical TBP geometry as phosphorane **26** (Table III), the phosphole ring occupies a strain-free axial-equatorial position. The weak axial intracyclic bond is thus selectively cleaved in the second step of the reaction. Subsequently, this reaction has been generalized to the monomeric 3,4-dimethylphospholium salts¹⁶⁶ (eq 95).

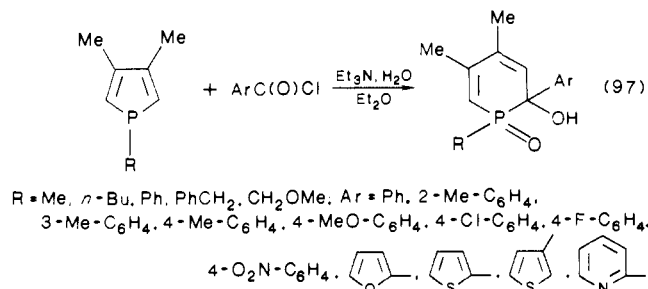


When one of the phosphorus substituents is a benzyl group, the hydrolysis of the phospholium salt mainly follows another path that involves the cleavage of the phosphorus-benzyl bond¹⁸⁶ (eq 96). There is an obvious parallel between this reaction and the reaction depicted in eq 93.



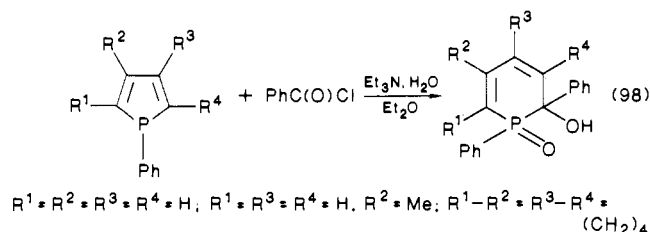
7. Ring Expansions

The only general one-step ring-expansion reaction of phospholes was discovered by Mathey.¹⁸⁷ It involves the hydrolysis of a mixture of phosphole, aromatic acid chloride, and triethylamine and yields a 2-hydroxy-1,2-dihydrophosphinine oxide. This reaction proceeds especially well with 3,4-dimethyl-substituted phospholes^{23,82,187-190} (eq 97). The ring expansion fails when

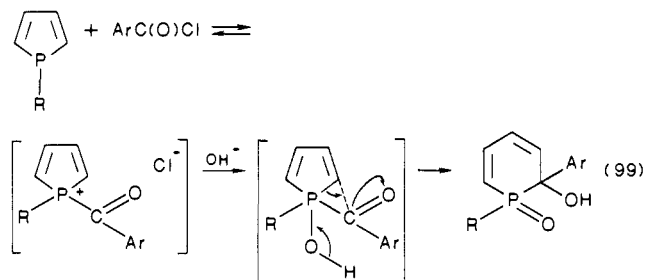


R or Ar is too bulky and when the aromatic acid chloride is replaced by an aliphatic derivative. The stere-

ochemistry of the final product is unknown but, according to ³¹P NMR spectroscopy, only one isomer is produced. Other phosphole substitution patterns can be used^{23,82,177} (eq 98). The most likely mechanism

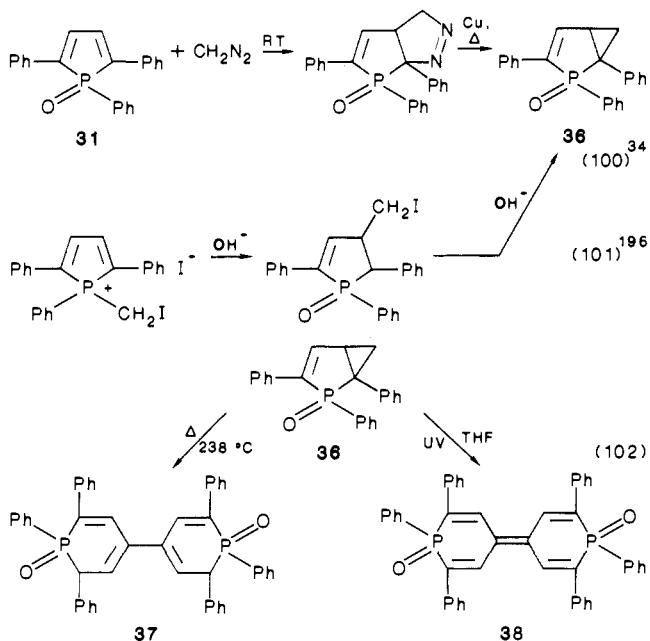


involves the hydrolysis of a transient acylphospholium salt (eq 99). Here again, the reaction is controlled by

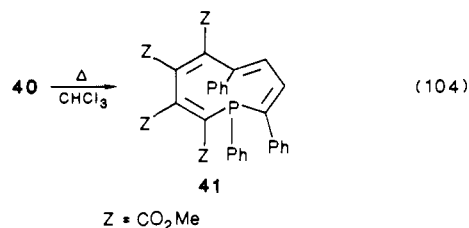
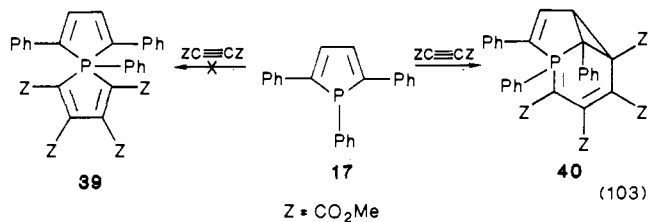


the cyclic strain of the phosphole ring. This explains why this ring expansion can be generalized to other strained phosphorus heterocycles including phosphindoles,^{191,192} dibenzophospholes,^{193,194} and phosphetanes.¹⁹⁵ One of the most interesting aspects of this reaction is that it can serve as a versatile starting step for the conversion of phospholes into phosphinines (see Section IV.A).

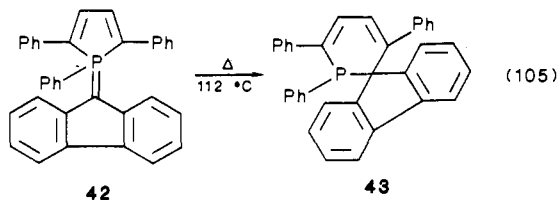
Various other ring-expansion techniques have been applied to the phosphole system but in each case, with limited success and generality. The formal cyclopropanation of one of the two double bonds of 1,2,5-triphenylphosphole oxide (**31**) was achieved by the two routes depicted in eq 100 and 101.^{34,196} Thermal and photochemical decompositions of the bicyclic oxide **36** then led to the ring-expanded products **37** and **38** (eq 102).¹⁹⁷



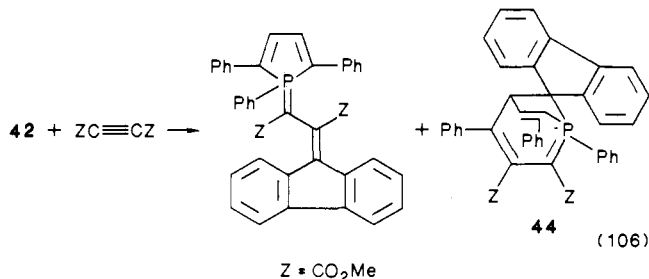
The reaction of dimethyl acetylenedicarboxylate with tertiary phosphines has already been discussed as a possible route to *2H*-phosphole derivatives (see Section I.B). The same reaction applied to 1,2,5-triphenylphosphole (17) was first thought to lead to the spirobicyclic phosphole 39.¹⁹⁸ The correct structure was later shown to be 40¹⁹⁹ (eq 103). In boiling chloroform, 40 rearranges to give a *cis,cis,trans,cis*-phosphonin 41¹⁹⁹ (eq 104). Much more recently, two other expansions



of the 1,2,5-triphenylphosphole ring have been described.^{200,201} It was first shown that the 1,2,5-triphenylphosphole ylide 42 undergoes upon heating a Stevens rearrangement leading to 43²⁰⁰ (eq 105). Then,



sometime later, it was shown that the same ylide 42 reacts with dimethyl acetylenedicarboxylate to yield *inter alia* a ring-expanded product 44²⁰¹ (eq 106). The



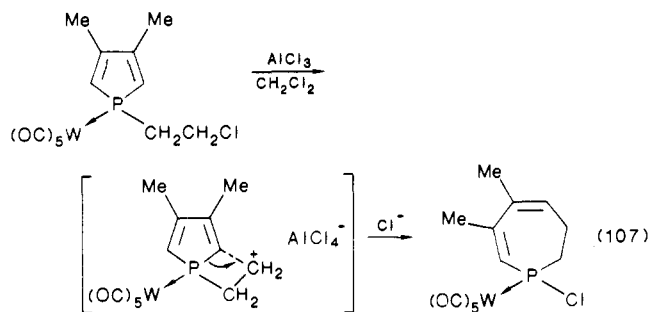
structures of 43 and 44 were checked by X-ray analysis. Compound 44 is thought to be formed through the preliminary rearrangement of 42 into 43 followed by the reaction of 43 with acetylenedicarboxylate.

Finally, other authors have very recently discovered a technique for converting the phosphole into the 6,7-dihydrophosphepine ring²⁰² (eq 107).

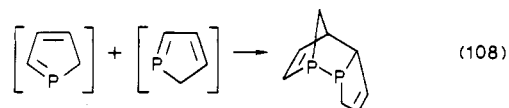
B. 2H-Phospholes

Dimerization and Reactivity toward A-H Compounds, Dienes, and Dienophiles

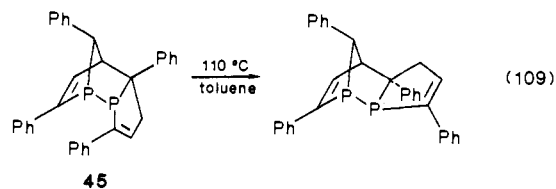
Even when they are generated at low temperature via the protonation of phospholyl anions (see Section I.B), dicoordinate *2H*-phospholes are unstable and instantly



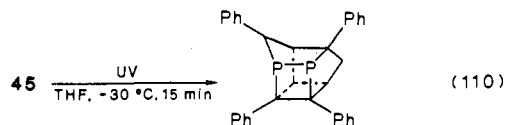
dimerize. This dimerization follows two different routes according to the substitution pattern of the ring. Broadly speaking, when the overall steric hindrance of the nucleus is low, a [4 + 2] cycloaddition takes place between the dienic system and the P=C double bond (eq 108). In one case, it has been possible to perform



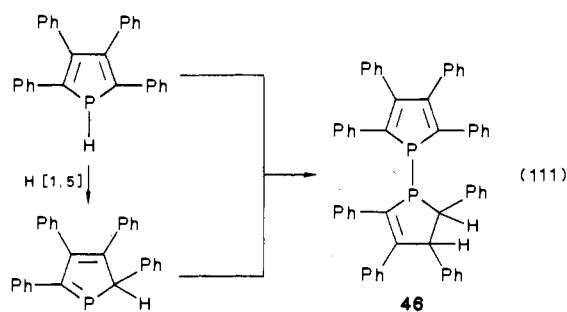
the X-ray crystal structure analysis of such a dimer.²⁰³ This dimer has an endo junction, a weak P-P bond (2.24 Å versus 2.21–2.22 Å for a normal P-P bond length), and a weak C-C bridge between the two phosphole units (1.58 Å versus 1.54 Å for a normal C-C single bond length). These data suggest that this dimerization is reversible upon heating and this is indeed the case. Around 100 °C, the kinetic endo dimer gives the thermodynamic exo dimer obviously via the monomeric *2H*-phosphole⁴ (eq 109). Thus, it is clear that



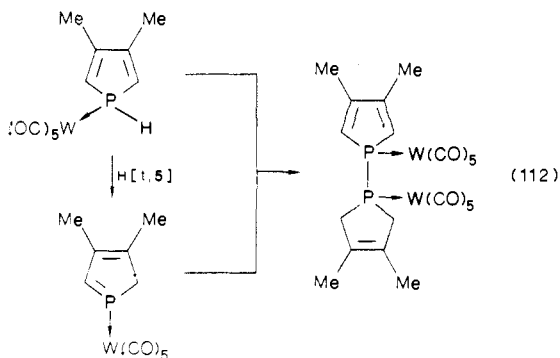
these isolable [4 + 2] P-P bonded dimers can be used as sources of the corresponding monomers. The kinetic endo dimers have another interesting property: they can be converted into novel cage compounds under UV irradiation⁴ (eq 110). When now the steric hindrance



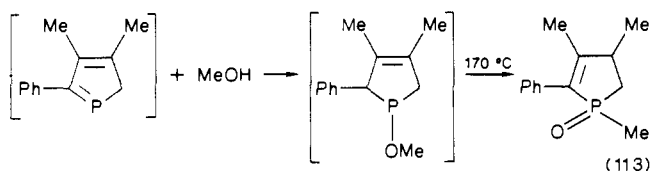
of the phosphole ring is high, the P-H phosphole that serves as a precursor for the *2H*-phosphole has a notable lifetime at room temperature and is able to trap the *2H*-phosphole via the addition of its P-H bond onto the P=C bond⁴ (eq 111). 3,4-Dimethyl-*2H*-phosphole,



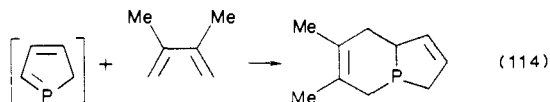
which normally follows the [4 + 2] pathway, appears to follow the P-H + P=C pathway when the 1H-phosphole is stabilized by P complexation²⁰⁴ (eq 112).



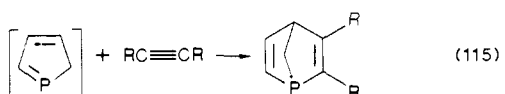
From another standpoint, it is clear that the P=C double bond of 2H-phospholes is able to add a wide range of A-H compounds but, apart from secondary phosphines, only alcohols have been used for such a purpose⁶⁸ (eq 113). In fact, by far the most interesting



reactions of 2H-phospholes involve external dienes or dienophiles. With conjugated dienes, a [2 + 4] cycloaddition is observed^{4,68,203} (eq 114). With alkynes,



1-phosphanorbornadienes are obtained through [4 + 2] cycloaddition^{4,68,203} (eq 115). The structure of one such

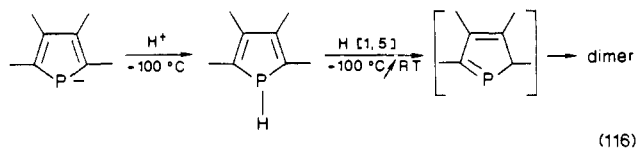


phosphanorbornadiene has been studied by X-ray analysis.⁶⁸ These bicyclic species can serve as starting points for the synthesis of phosphinines (see Section IV.A).

C. Phospholyl Anions

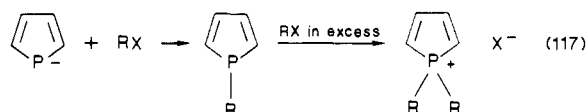
Nucleophilic Properties of Phosphorus

All the reactions of phospholyl anions so far reported take place at phosphorus. The protonation of 2,5-diphenyl- and 2,3,4,5-tetraphenylphospholyl anions was initially claimed to yield the corresponding stable P-H phospholes.³⁹ This statement was much later shown to be erroneous.⁴ In fact, the protonation products of these anions are the 2H-phosphole dimers 45 (eq 109) and 46 (eq 111), respectively (see Section III.B). A careful study by ³¹P NMR spectroscopy of the protonation of phospholyl anions, however, clearly demonstrated that the initial protonation site is phosphorus.⁴ The resulting P-H phospholes are quite unstable and rearrange through H migration to give transient 2H-phospholes, which then dimerize⁴ (eq 116) (see also Section I.B). The parent phosphole was thus characterized at -100 °C for the first time.⁴ Only 2,3,4,5-

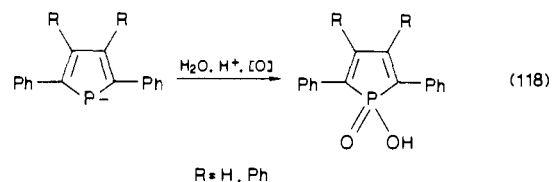


tetraphenylphosphole has a reasonable lifetime at room temperature (half-life ca. 0.5 h at 25 °C). It can be fully stabilized by P complexation with W(CO)₅.⁴ The aromaticity of phospholyl anions of course reduces their basicity. As a consequence, the 2,5-diphenyl and 2,3,4,5-tetraphenyl species do not react with neutral water, which means that their pK_a value is lower than 14.⁶⁹ On the contrary, the 3,4-dimethylphospholyl anion does react with water, thus illustrating the significant influence of the substitution pattern on the nucleophilicity of phosphorus. A similar effect has been noted with phospholes.

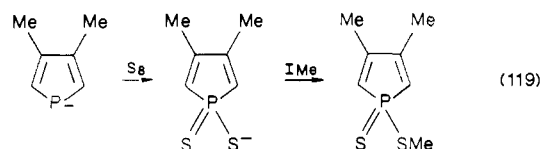
By far the most widely used reaction of phospholyl anions is their P-alkylation³⁹ (eq 117). Apart from



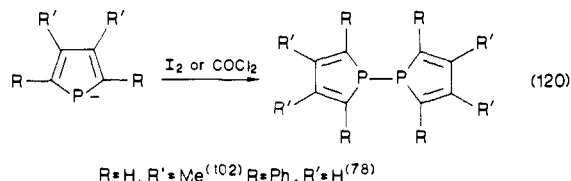
classical alkylating agents such as IMe or BrCH₂Ph, numerous other halocarbon derivatives have been used. Thus, according to the experimental conditions, 1,*n*-dihaloalkanes either yield 1-(*n*-haloalkyl)phospholes or 1,*n*-bis(phospholyl)alkanes.^{39,85,162,173,202} On the other hand, numerous functional haloalkanes have been successfully used including BrCH₂CO₂Et,^{39,79} ClCH₂CN,⁷⁹ BrCH₂CH₂CN,⁷⁹ BrCH₂C(O)Ph,⁷⁹ ClCH₂C(O)Me.⁷⁹ In two cases, the oxidative hydrolysis of phospholyl anions has been shown to yield the corresponding monomeric phosphoric acids^{36,39} (eq 118). Similarly, in one



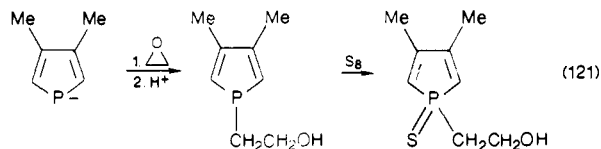
instance, sulfur has yielded the expected monomeric dithiophosphoric acid derivative²⁰⁴ (eq 119). The re-



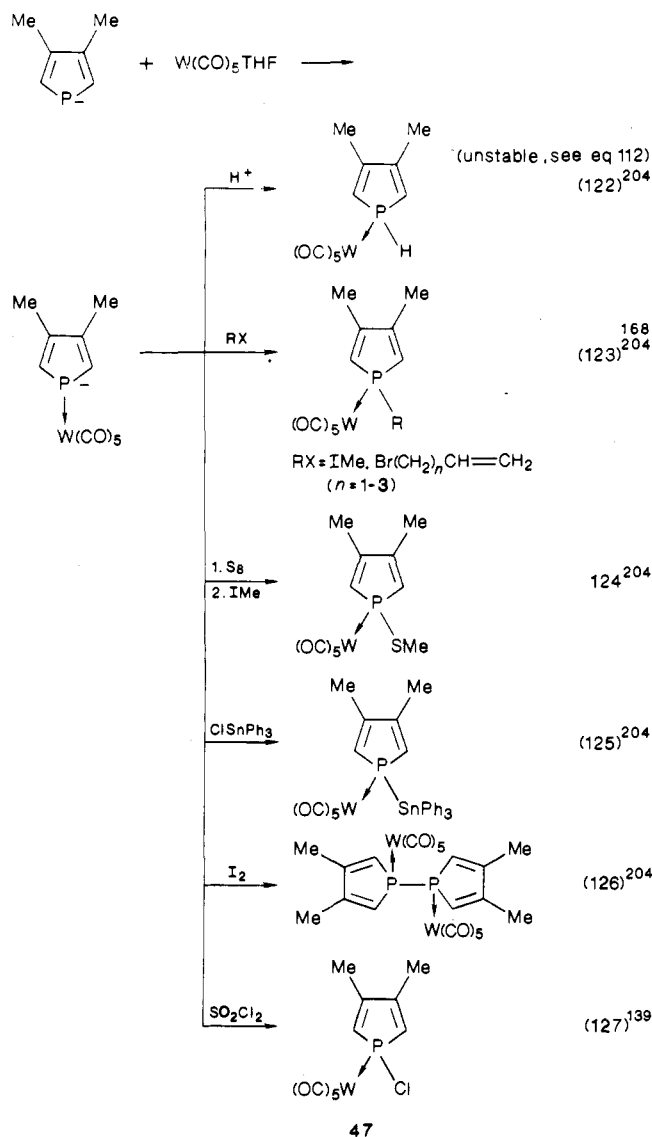
action of phospholyl anions with halogens under mild conditions generally gives the P-P bonded bis-phospholyls^{78,102} (eq 120). An excess of halogen may cleave the P-P bond (see eq 49).



Finally, the reaction of phospholyl anions with ethylene oxide has been reported in one case⁷⁹ (eq 121). Before leaving the subject, it must be noted that the



chemistry of phospholyl anions has also been investigated in the coordination sphere of tungsten. A close parallelism is generally observed between the behaviors of free and complexed anions (eq 122-127). Compound 47 has no stable equivalent in the free state.



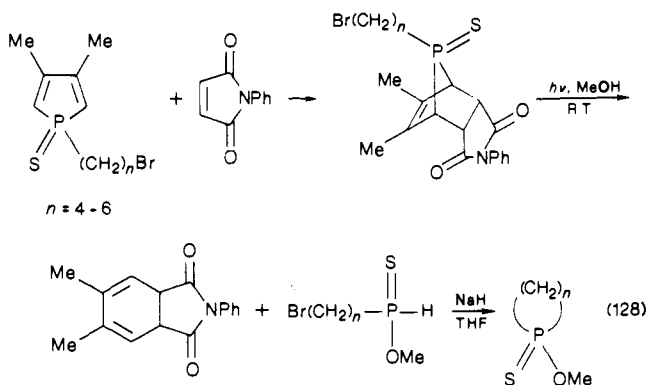
IV. Phospholes as Synthons

A. Synthesis of Other Phosphorus Heterocycles

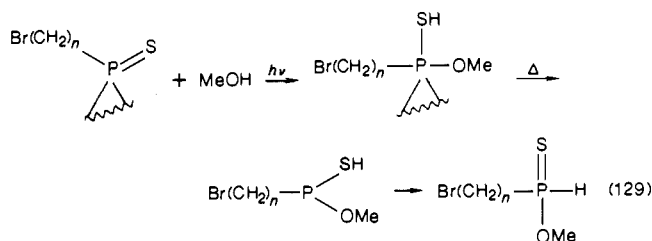
The versatility of phospholes as building blocks for the synthesis of other organophosphorus species is already quite obvious when looking at the preceding sections. It must be remembered here that the best known precursors of phosphinidene oxides [RP=O] (eq 75), sulfides [RP=S] (eq 66, 67, and 69), and complexes [RP=M] (eq 74) have all been made from phospholes. Similarly, efficient precursors of metaphosphates [ROPO₂], metaphosphonates [RPO₂], and metaphosphoramidates [R₂NPO₂] have also been obtained from phospholes.^{151,152} The chemistry of these transient

species is clearly outside the scope of this review. On another side, numerous phosphorus heterocycles have already been mentioned in the course of this review especially in Sections III.A.4 and III.A.7. However, some of the most noteworthy applications of phospholes in the synthesis of other phosphorus heterocycles have escaped notice until now and deserve some comments in order to illustrate the tight connection between phosphole chemistry and the rest of phosphorus heterocyclic chemistry.

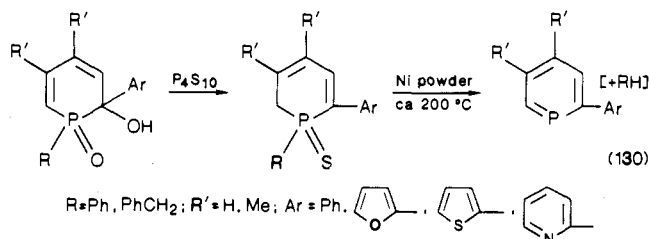
As a first example, a general scheme for preparing saturated carbon-phosphorus heterocycles must be mentioned¹⁶² (eq 128). In its key step, it formally



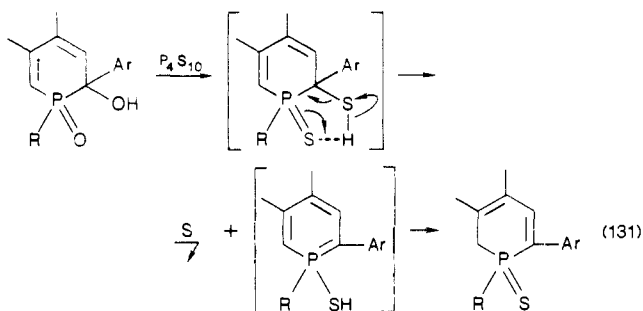
involves the addition of MeOH onto a phosphinidene sulfide [Br(CH₂)_nP=S]. In fact, the collapse of the phosphorane bridge probably involves a transient P^V species as suggested by the work of Quin on a similar system²⁰⁵ (eq 129).



Phospholes have also proved to be convenient starting points for the synthesis of phosphinines. The first technique relies on the ring expansion of phospholes by reaction with aromatic acyl chlorides and water (see eq 97). The ring-expanded products are in turn allowed to react with P₄S₁₀ (or with the so-called Lawesson reagent [p-MeOC₆H₄PS₂]₂) to give a 1,2-dihydrophosphinine sulfide. Then, this sulfide is pyrolyzed with nickel powder^{82,189,190} (eq 130). A possible mech-

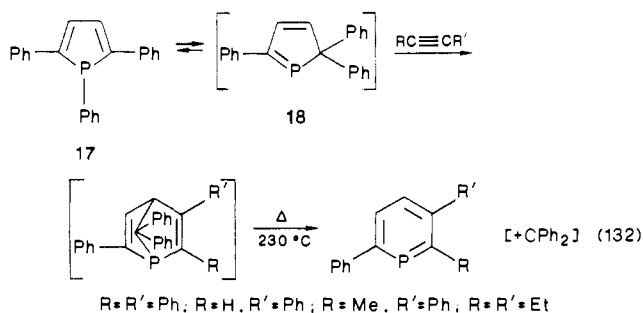


anism has been proposed for the curious sulfurization step⁸² (eq 131). The driving force for the extrusion of sulfur would be the extra stabilization gained when the 1,2-dihydrophosphinine sulfide is converted into the corresponding λ⁵-phosphinine. The scope of this phosphole → phosphinine conversion scheme is rather



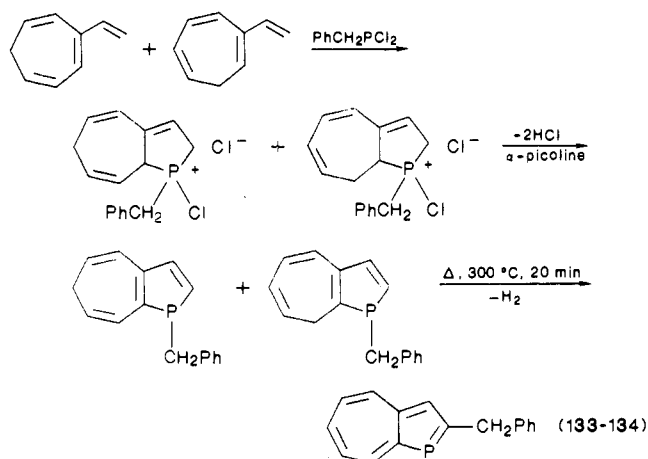
wide. It has allowed the synthesis of the first known phosphorus analogue of a 2,2'-bipyridyl¹⁹⁰ and can be applied to phosphinodoles¹⁹² and dibenzophospholes¹⁹⁴ for the synthesis of isophosphinolines and phosphaphenanthrenes.

The second technique relies on the 1*H*- to 2*H*-phosphole thermal conversion via the migration of a phenyl substituent from phosphorus to carbon (see eq 28). The 2*H*-phosphole thus obtained is allowed to react with alkynes. Thermal decomposition of the resulting 1-phosphanorbornadienes (see eq 115) affords the corresponding phosphinines⁸³ (eq 132). This one-pot technique is especially simple to use.



The third technique relying on the reaction of a monomeric phosphole sulfide with a phosphalkyne¹⁷⁶ has already been described (see eq 76).

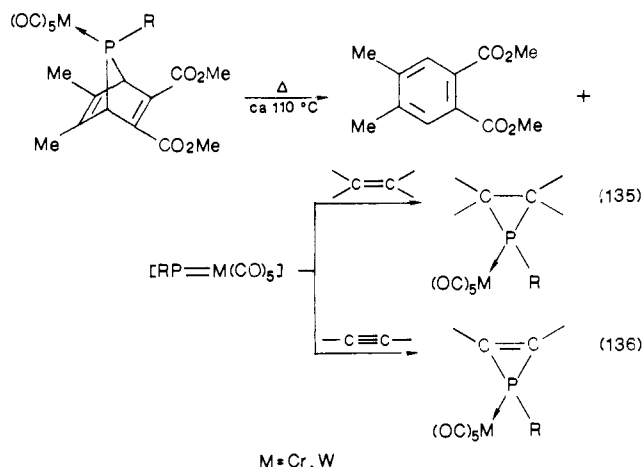
The first synthesis of a 1-phosphaazulene as devised by Märkl²⁸ also involved the preparation of a phosphole as an intermediate step (eq 133–134). The first two



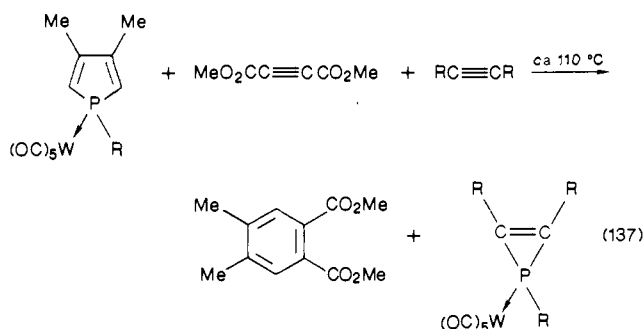
steps are classical (see eq 1) and the thermal benzyl [1,5] shift observed during the last step closely parallels an already described chemistry (see eq 27 and 28). The 1-phosphaazulene thus obtained is the first known aromatic phosphorus heterocycle with 10 π -electrons.

Finally, it must be noted that phospholes can also serve as an indirect source of three-membered carbon-

phosphorus heterocycles via transient terminal phosphinidene complexes. These complexes are generated by thermolysis of the appropriate 7-phosphanorbornadiene complexes (see eq 74) and easily react with C=C double bonds²⁰⁶ and C≡C triple bonds²⁰⁷ (eq 135 and 136). The phosphirane and phosphirene com-



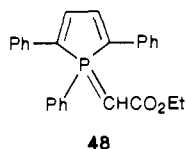
plexes thus obtained can be decomplexed to give the corresponding free species.²⁰⁸ Besides, it is possible to perform in one pot the whole sequence leading from phospholes to the three-membered rings²⁰⁹ (eq 137).



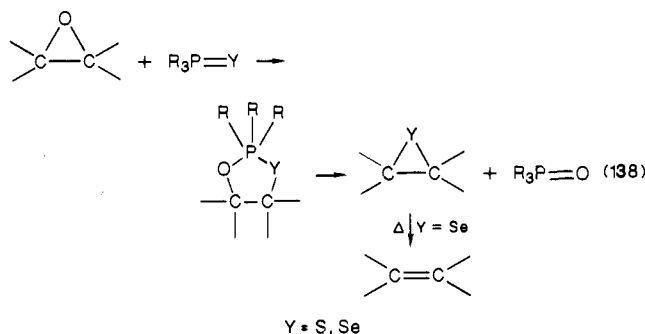
This kind of chemistry has been reviewed elsewhere.¹⁷² It is interesting to remark that the first known phosphirenes have been discovered by using this phosphole route.

B. Uses in Synthetic Organic Chemistry and in Homogeneous Catalysis

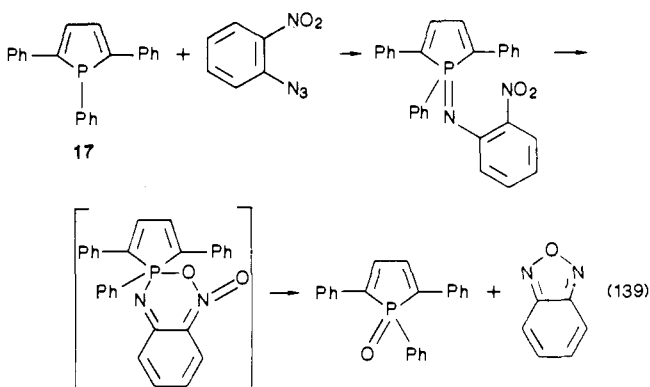
The rationale behind the use of phospholes in organic synthesis is that most of the reactions involving phosphorus derivatives imply the formation of transient phosphoranes as the key step. The cyclic strain of the phosphole nucleus (CPC intracyclic angle close to 90°; see Section II.A.1) is supposed to favor this formation since strain is suppressed in the phosphorane TBP structure. It is quite clear that any kind of strained cyclic phosphine with an intracyclic angle close to 90° can be used in lieu of phospholes for such a purpose. In fact, most of the synthetic applications of strained phosphines in organic synthesis were developed with the readily available dibenzophospholes. However, some results were also obtained with phospholes. For example, it was shown that ylide 48 reacts more sluggishly with carbonyl compounds and gives more *cis* olefin than its Ph₃P analogue.²¹⁰ This is rationalized as follows: the rate-determining formation of the betaine is slowed down due to the reduced tendency of



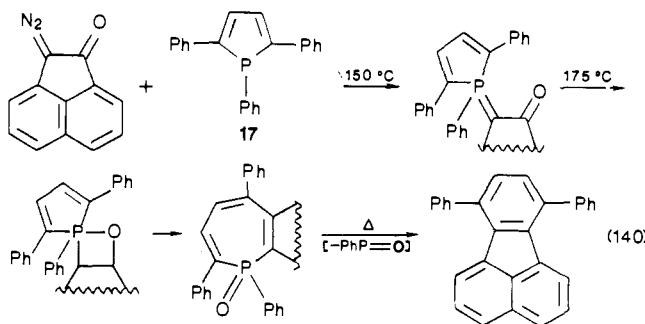
1,2,5-triphenylphosphole to give quaternary salts; on the contrary, the collapse of the betaine through the corresponding oxaphosphetane is accelerated by the ring strain, thus reducing the cis \rightarrow trans olefin equilibration. In the same vein, the conversion of epoxides into episulfides or olefins through reaction with phosphine sulfides or selenides, respectively, is highly favored when Ph_3PS or Ph_3PSe is replaced by its monomeric phosphole analogue derived from 15²¹¹ (eq 138). Various



other results have been obtained by the group of Cadogan. For example, a synthesis of benzofurazans by reaction of 17 with *o*-nitrophenyl azides was devised^{37,212} (eq 139). No similar reaction takes place with Ph_3P and $(\text{EtO})_3\text{P}$.



The formation of 7,10-diphenylfluoranthene by reaction of 17 with 1-diazoacenaphthen-2-one was also described.²¹³ The mechanism was initially thought to involve acenaphthene,²¹³ but this proposal was subsequently withdrawn²¹⁴ (eq 140). Finally, the formation



of 1,4-diphenylanthracene from *o*-bromophenol and 17, initially thought to proceed via the reaction of benzyne with 1,2,5-triphenylphosphole oxide, was later

shown to result from the reaction of HBr with 17.²¹⁵

Phospholes have also found various uses in homogeneous catalysis. For example, some phosphole complexes with ruthenium have been shown to efficiently catalyze the hydrogenation of 1-heptene at room temperature and pressure.²¹⁶ The complex of 17 with PdCl_2 has been used for the catalysis of some carbonylation reactions.²¹⁷ Various phosphole complexes with cobalt and rhodium carbonyls have been proposed as catalysts for the hydroformylation of olefins.²¹⁸⁻²²¹

Acknowledgments. A part of the work described in this review has been carried out in the laboratory of the author. The author gratefully thanks his co-workers whose names are cited in the references for their dedicated work and Françoise Hervagault for the preparation of the manuscript and for the drawing which illustrates this work. This research has been supported by the Centre National de la Recherche Scientifique (CNRS) and by the Société Nationale des Poudres et Explosifs (SNPE). Their help is gratefully acknowledged.

Registry No. 1*H*-Phosphole, 288-01-7; 2*H*-phosphole, 23630-06-0.

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