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RECENT ADVANCES IN THE STAUDINGER REACTION

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CONTENTS

1. INTRODUCTION

Ten years ago we published the first review[1] on the Staudinger reaction: the imination reaction of tervalent phosphorus derivatives with organic azides discovered in 1919.[2] For the past decade, extensive investigations have been carried out in this field. They explored the concept of the reaction and considerably widened its synthetic utility. In addition to $\lambda^3\sigma^3$ phosphorus compounds, compounds containing P atoms of different coordinations and valencies as well as other organoelement compounds were found to undergo the Staudinger imination. The molecular structures of intermediate phosphazides in the classical Staudinger reaction have now been unequivocally established. Some new rearrangements of imination products have been observed and studied. Impressive successes were also achieved in the synthesis of heterocyclic compounds especially via the aza-Wittig reaction.

2. THE CLASSICAL STAUDINGER REACTION

The Staudinger reaction in its classical form is a two-step process involving the initial electrophilic addition of an azide to a P^{III} centre followed by dinitrogen elimination from the intermediate phosphazide **A** giving the iminophosphorane **B**.

$$\text{—P} + N_3R \longrightarrow \underset{\mathbf{A}}{\text{—PN}_3\text{R—}} \longrightarrow \underset{\mathbf{B}}{\text{—P=NR—}} + N_2 \qquad (1)$$

Usually, the imination proceeds smoothly, almost quantitatively, without noticeable formation of any side products. The phosphorus and azide components of the Staudinger reaction were previously characterized in detail.[1] In the following section the new reagents recently studied in this reaction are briefly surveyed.

2.1. *Reactants*

2.1.1. *Phosphorus(III) compounds.* In Chart 1 some typical examples selected from studied

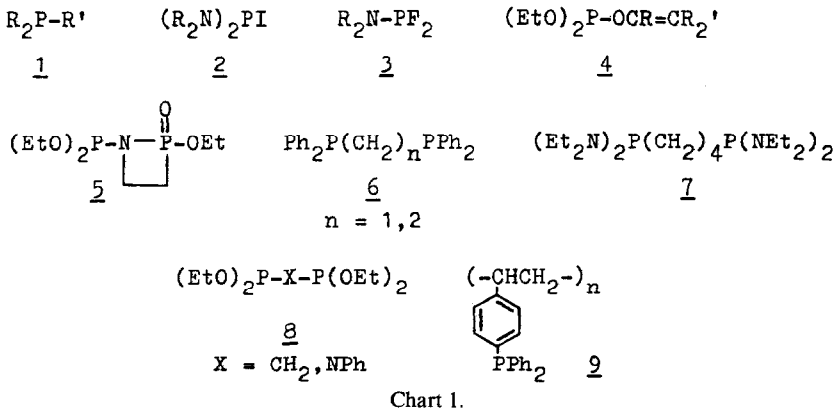
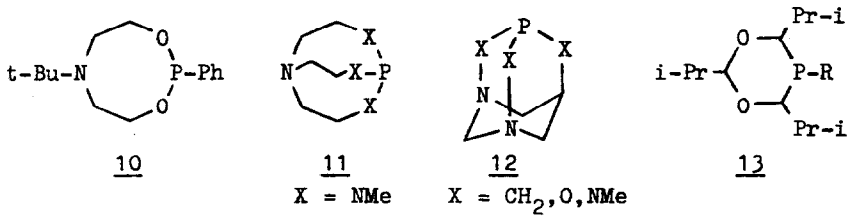


Chart 1.

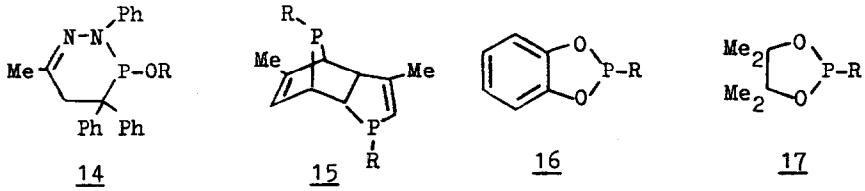
classes of acyclic tervalent phosphorus compounds are presented. Among them are asymmetric phosphines[3–7] **1**, halogenated phosphines,[8–12] **2**[8] and **3**,[11] phosphorus acid esters, vinyl esters,[13–15] amides[16,17] **4**[15] and **5**,[17] as well as their bisphosphorus analogues, **6**,[18,19] **7**,[20] **8**,[21,22] and polymeric phosphines **9**.[23]

The cyclic derivatives of three-coordinate phosphorus also constitute an extensive group (Chart

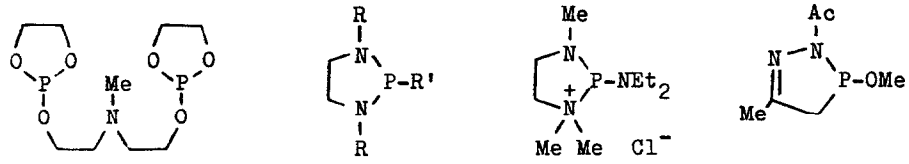


10 11 12 13

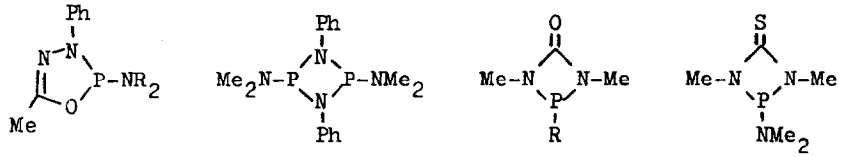
X = NMe X = CH_2, O, NMe



14 15 16 17



18 19 20 21



22 23 24 25

Chart 2.

2) including dioxazaphosphocine[24] **10**, phosphatrane[25] **11**, phospha-adamantanes[26,27] **12**, dioxaphosphorinanes[28] **13**, diazaphosphorines[29] **14**, phosphole dimers[30] **15**, benzodioxaphospholes[31,32] **16**, dioxaphospholanes[33–36] **17**[33] and **18**,[35] diazaphospholidines[37] **19**, diazaphospholidinium salt[38] **20**, diazaphosphole[39,40] **21**, oxadiazaphospholes[41] **22**, diazadiphosphetidine[42] **23**, diazaphosphetidinones[43] **24**, and others. It is of interest that diazaphosphetidinethione **25**, the sulfur analogue of **24**, is iminated with trimethylsilyl azide at thione carbon but not at the phosphorus(III) site.[44]

2.1.2. *Azides.* In the Staudinger reaction, alkyl, aryl, arenesulfonyl, acyl, phosphoryl or triorganyl azides are traditionally used as azide components. This group has been considerably widened. In Chart 3 some new examples are shown. They comprise azetidinyl azide[45] **26**, cyanazide[46] **27**, sulfonyl azides[47–50] **28**,[47] **29**,[48] and **30**,[49] phosphoryl azides **31**,[51–56] **32**,[57] and **33**,[57,58] azidophosphonium salt **34**,[59] azidospirophosphoranes **35**,[58] **36**,[60,61] and **37**,[62] tantalum tetrachloride azide **38**,[63] and the azidoborane **39**.[64]

Nitroyl azides, e.g. **40** (Chart 3), form an interesting subgroup which is used for preparation of spin labels by the Staudinger reaction, in order to study various biological systems.[65] Azido-

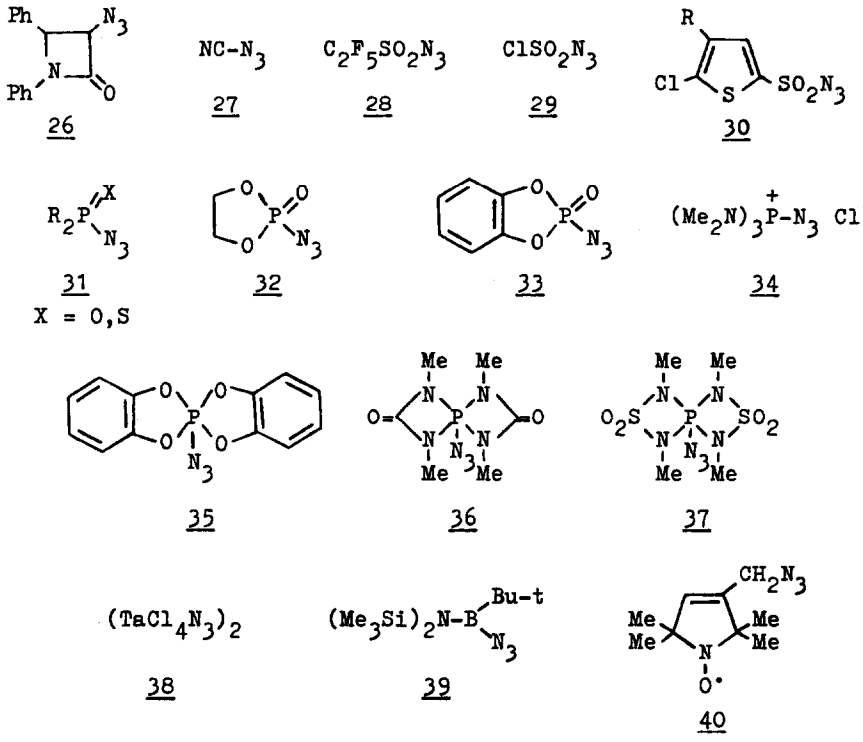
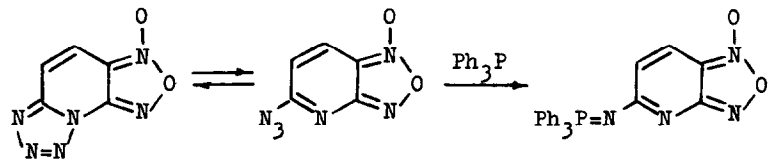


Chart 3.

pyridines[66] and azidopyridazines[67] having an azido-group incorporated into a tautomeric tetrazole cycle undergo the Staudinger conversion (eqn 2).[66]



(2)

It was proposed to use hydrazines, $RNHNH_2$, as the precursors of the azide components in the synthesis of iminophosphoranes. The hydrazines are catalytically converted to azides (on clay-supported ferric nitrate) and then, without isolation, condensed with phosphorus(III) reagents.[68,69] A similar approach to imination with azides $(RO)_2P(O)N_3$ *in situ* was utilized in a system presented in equation (3) where the combination of the Atherton–Todd and Staudinger reactions was realized in a one-pot version.[70]

$$\begin{aligned}
&(RO)_2P(O)H + CCl_4 \longrightarrow (RO)_2P(O)Cl\\
&(RO)_2P(O)Cl + NaN_3 \longrightarrow (RO)_2P(O)N_3\\
&(RO)_2P(O)N_3 + (R'O)_3P \longrightarrow (RO)_2P(O)\text{-}N{=}P(OR')_3\\
&\overline{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad}\\
&(RO)_2P(O)H + (R'O)_3P + CCl_4 + NaN_3 \longrightarrow (RO)_2P(O)\text{-}N{=}P(OR')_3
\end{aligned} \tag{3}$$

There are numerous examples of imination with bis-, tris-, and polymeric azides (Chart 4).

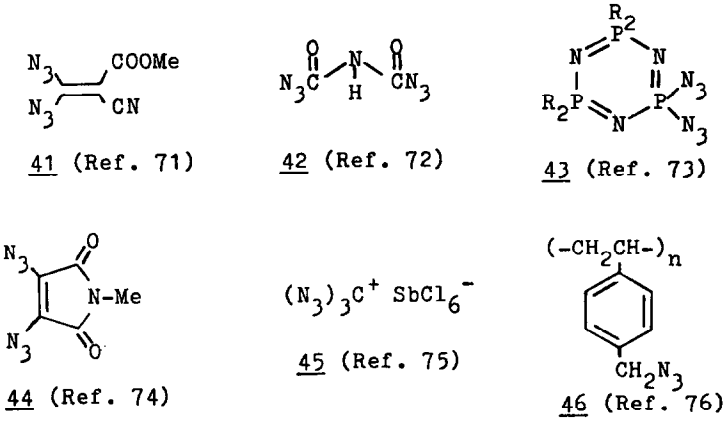
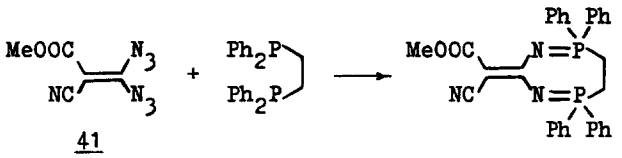


Chart 4.

Depending on reactant ratios, one or two N_3 groups of a bisazido component can participate in the reaction. In the last case, as shown for bisazide **41**, the imination can lead to a cyclic product.[71]



(4)

2.1.3. *Azidophosphines.* Compounds of this type contain in the same molecule a P^{III} atom and an azido group. Therefore, in the Staudinger reaction, they can act as bifunctional reagents. Such compounds are usually prepared by the exchange reaction between appropriate phosphochloridites and Me_3SiN_3 or metal azides.[77] Chart 5 illustrates some representatives of this chemical class, i.e. **47–53**.

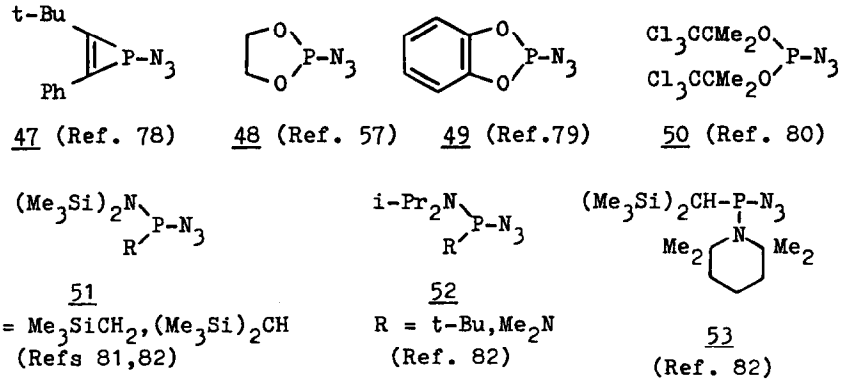
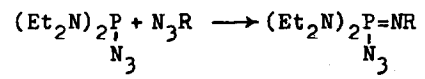


Chart 5.

The thermal autocondensation of azidophosphines was supposed to proceed through an intermediate phosphonitrile, $R_2\overset{+}{P}{=}\overset{-}{N}$, providing polyphosphazenes.[82] In the presence of another monofunctional azide, the usual Staudinger imination of the P^{III} site takes place.[83]

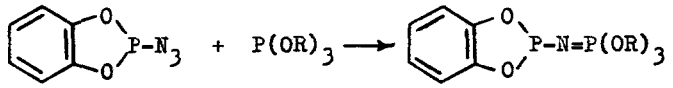


(5)

54 R = Ph, Tos

In a similar fashion the azidophosphites **48**,[57] **50**,[80] and $(i\text{-}Pr_2N)_2PN_3$ **(55)**[84] react with phenyl azide. Compound **49** does not, however, interact with PhN_3.[57] In the system **55**, Me_3SiN_3, the phosphorus imination under thermal conditions is not observed, but on uv irradiation it does proceed, presumably by a nitrene mechanism.[84,85]

In equation 6, the azidophosphite **49** acts as an azido component.[79] However, the azides **48** and **54** do not react with triethyl phosphite.[57,79]



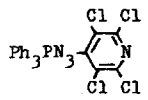
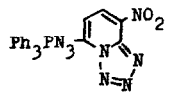
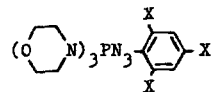
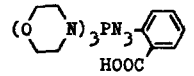
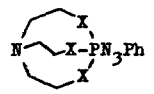
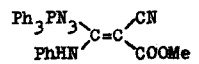
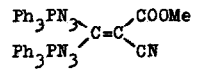
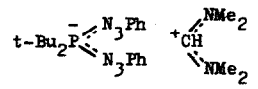
49 R = Et, Pr (6)

The behavior of these bifunctional reagents in the Staudinger reaction is presumably determined by their relative phosphorus nucleophilicity and azide nitrogen electrophilicity.

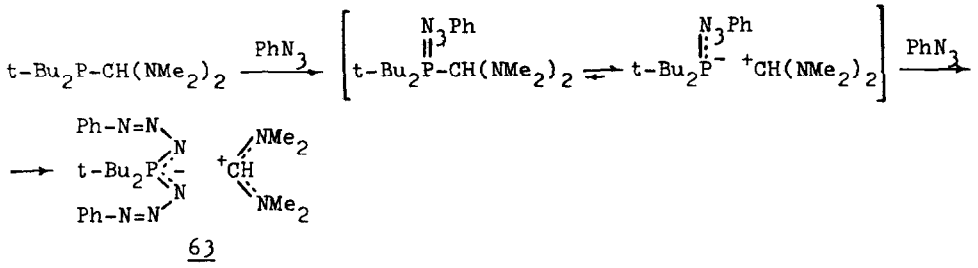
2.2. *Intermediate phosphazides in the Staudinger reaction*

The intermediate formation of phosphazides in the Staudinger reaction is well documented. Many phosphazides have been isolated and characterized (ref. 1). In Table 1 some recent examples are listed. The unusual phosphazide **63** in Table 1 was synthesized as in equation (7).[91] There have

Table 1. Phosphazides

Compound	Phosphazide		Yield, %	M.p. °C (dec)	Ref.
56			88	96–98	86
57			88	98–100	66
58a		X = NO_2	89	155–156	87
58b		X = Br	90	186–189	88
59			96	147–148	89
60		X = NMe	68	163–165	25
61			68	104	90
62			76	62	71
63			70	-	91

been many reports on the spectral detection (^{31}P, ^{15}N, ^{13}C NMR) of intermediate phosphazides in the Staudinger process (refs 66, 73, 84, 92).



(7)

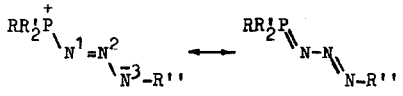
63

2.2.1. *Molecular structure of phosphazides.* The structure of phosphazides was a point of protracted controversy (ref. 1). Recently investigators have succeeded in elucidating the important features of the molecular structure for five phosphazides by X-ray crystallography.[87,89,93–96] The first phosphazide investigated by this method was $Ph_3PN_3C_6H_4Me$-p;[95] however, it was studied as a ligand in the metal complex $WBr_2(CO)_3(Ph_3PN_3C_6H_4Me$-p).

Selected X-ray structural data for phosphazides are listed in Table 2. It was found that the fragment PN_3 in a phosphazide is acyclic, that is the azide is added to the P^{III} site by its terminal nitrogen atom. The chain PN_3C is nearly planar and has the (*E*)-configuration with respect to the central N^1–N^2 link which exhibits, partially, double bond characteristics. In the sequence **58**, **64**, **65**, and **66** the N^1–N^2 bond order decreases (with increase in length) and the thermal stability of the molecules is reduced. This trend is partly determined by the fact that for elimination of nitrogen from a phosphazide, the rotation of its terminal groups around this bond is required (eqn 8).

The phosphorus atoms in phosphazides have partial phosphonium character. The negative charge from the N^3 atom is delocalized to the aromatic ring (R″) which in compounds **58a**, **64**, **65**, and **67** is twisted out of the plane PN_3C by 32.2°, 9°, 7.8° or 11°, respectively. The phosphorus positive charge in all cases is delocalized much less effectively.

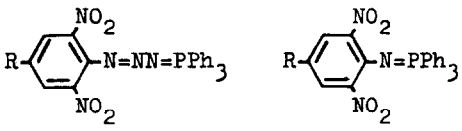
Table 2. Selected X-ray structural data for phosphazides



Compound	R	R′	R″	Bond lengths (Å)				Angles (°)			Ref.
				P–N^1	N^1–N^2	N^2–N^3	N^3–C	PN^1N^2	$N^1N^2N^3$	N^2N^3C	
58a	O(N-)	O(N-)	2,4,6-$(O_2N)_3C_6H_2$	1.638	1.299	1.317	1.368	119.1	112.0	112.2	87
64	Ph	Ph	2-$HOOCC_6H_4$	1.651	1.328	1.279	1.413	109.52	112.97	114.80	89
65	O(N-)	Et_2N	Ph	1.623	1.342	1.273	1.423	114.77	112.6	112.3	93
66	Me_2N	Me_2N	$HO(CH_2)_3$	1.615	1.375	1.256	1.472	111.7	112.1	111.2	94
67*	Ph	Ph	4-MeC_6H_4	1.672	1.365	1.280	1.424	112.9	103.8	116.3	95

* In the complex $WBr_2(CO)_3(Ph_3PN_3C_6H_4Me$-p).

2.2.2. *Chemical properties of phosphazides.* pK_a Measurements have shown that phosphazides **68** are less basic than the corresponding iminophosphoranes **69**.[97]

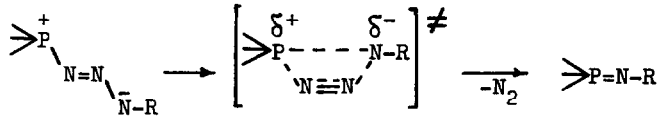


68 **69**

R = MeO, H, Cl, CF_3, NO_2

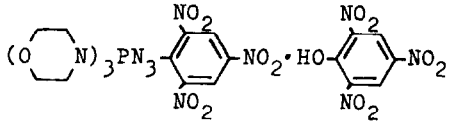
As the parameters ρ in the Hammett correlations of pK_a values for **68** are substantially smaller than for **69**, it was concluded that for the phosphazides **68**, protonation occurs at the N atom adjacent to phosphorus.[97]

In a chemical respect, phosphazides have been inadequately studied. Only their thermal conversion into iminophosphoranes by the mechanism in equation 8 was investigated in detail.[1] The sensitivity of thermolysis kinetics for the phosphazide **56** (Table 1) to a solvent polarity is rather weak.[86] This is perhaps due to the low degree of charge separation in the transition state (eqn 8).



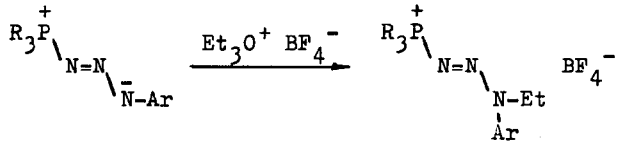
(8)

Weak acids, for example picric acid, give complexes with phosphazides in solution. This was utilized in the kinetic studies of the Staudinger reaction.[98] A stable complex of this kind, **70**, was isolated, but its structure was not determined.[96] Strong acids, such as trifluoroacetic acid, cleave phosphazides **68** giving anilines and triphenylphosphine oxide.[99]



70

The negative charge at N(Ar) atom in phosphazides implies the possibility of *N*-alkylation. Indeed, such a reaction has been realized (eqn 9).[96,100]



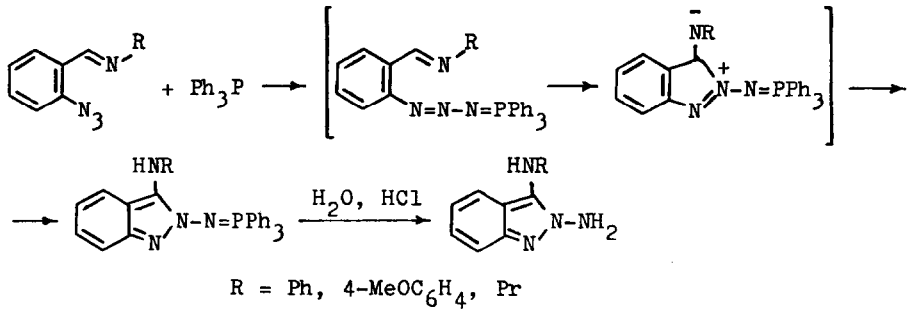
(9)

71a-c

a R = $O(CH_2CH_2)_2N$- Ar = 2,4,6-$(NO_2)_3C_6H_2$
b R = $O(CH_2CH_2)_2N$- Ar = 2,4,6-$Br_3C_6H_2$
c R = Ph Ar = 2,4,6-$(NO_2)_3C_6H_2$

It proceeds in a regio- and stereo-specific manner with retention of the nitrogen triad. The molecular structure of the product **71a** was confirmed by X-ray analysis.[100]

Recently, the first example of intramolecular cyclization of an intermediate phosphazide was observed.[101,102]

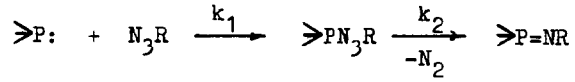


(10)

R = Ph, 4-MeOC$_6$H$_4$, Pr

2.3. *Mechanism of the Staudinger reaction*

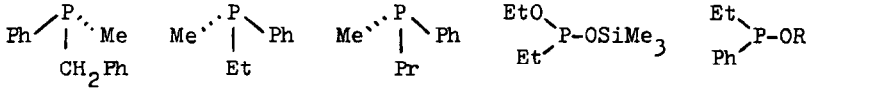
The main features of the Staudinger reaction mechanism have been discussed.[1] The imination is a two-step process which is started by electrophilic addition of the azide to tervalent phosphorus. The addition is not hindered, at least not by substituents at phosphorus, and its rate is controlled by the inductive influence of the substituents and by the azide electrophilicity.



(11)

The relation between the rates of the phosphazide formation (the second-order rate constant k_1) and its intramolecular decomposition (the first-order rate constant k_2) determines the overall kinetic order for the process (eqn 11).

2.3.1. *Stereochemical aspects.* For a number of phosphazides it was established[1] that the Staudinger imination proceeds with retention of the initial phosphorus stereoconfiguration. This finding was further confirmed for new examples including the optically active phosphines **72**,[103,104] **73**,[104] and **74**[105,106] (Chart 6). For the first time, the chiral esters of phosphorus(III) acids, e.g. **75**[107] and **76**,[108] were also used in such studies.

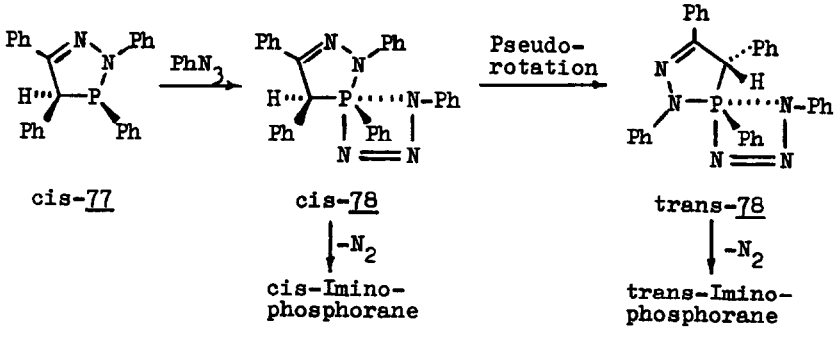


R(+)-72 S(-)-73 S(+)-74 75 (S)-,(R)-76

R = menthyl

Chart 6.

The *cis–trans* isomerization observed during imination of the diazaphosphole **77** was explained by pseudorotation of the intermediate spiroadduct **78** (Scheme 1).[109]



Scheme 1.

Table 3. Rate constants k_1 for imination of tri(n-butyl)phosphine with alkyl azides RN_3 (benzene, 30°C)[113]

R	E_S^o (R)	$k_1\ 10^2$, $M^{-1}s^{-1}$
n-Bu	-0.59	6.8
i-Pr	-0.85	2.4
c.-C_6H_{11}	-1.19	2.5
s-Bu	-1.53	2.2
t-$BuCH_2$	-1.94	4.3

The sterically unhindered behavior of a phosphorus site on azide attack (the first step in eqn 11) is reflected in a low sensitivity of the rate constants k_1 to the bulk of substituents at the P atom, in particular, adamantoxyl,[110,111] isoalkoxyl,[36] and *ortho*-substituted phenoxyl groups.[112] Some quantitative data on the steric shielding of the N_3 group in azides have also been obtained. Steric hindrance was shown not to be crucial by comparing the values of the rate constants k_1 for imination of tri(n-butyl)phosphine with alkyl azides (Table 3).[113]

It seems likely that the efficiency of intermediate phosphazide stabilization by steric crowding at a nitrogen terminus, at least with *ortho*-substituted aryl groups, is rather small.[86,88]

2.3.2. *Electronic effects of substituents at phosphorus.* The influence of substituents at phosphorus on the rate of the first imination step is mainly determined by their inductive effects.[1] This is reflected in the correlation equations (12a, b) where k_1 is the rate constant for imination of a phosphorus reagent with phenyl azide under the standard conditions (THF, 20°C) and $\Sigma\sigma_I$ is a sum of inductive parameters of the three groups attached to phosphorus.[114]

$$\log k_1 = 2.274 - 5.656\Sigma\sigma_I \tag{12a}$$

$$\Sigma\sigma_I = 0.405 - 0.176\log k_1 \tag{12b}$$

The relationship in equation 12b was used to calculate σ_I values for various groups at a phosphorus(III) atom.[110,114,115] In Table 4 some new σ_I constants evaluated by this method are summarized, in addition to the previously reported[1] list.

It may be noted that the inductive effect of vinyloxy radicals (entries 5–17, Table 4) is rather conservative with respect to electron-withdrawing substituents at α- or β-carbon and remains fairly constant, $\sigma_I = 0.50 \pm 0.03$. The bidentate 1,2-dioxy-substituents (entries 18–21, Table 4) exhibit considerably more inductive electron-withdrawing ability than a pair of corresponding alkoxy groups.

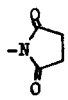
The correlation similar to that in equation 12b was also found in the system RPF_2–PhN_3. This correlation has been used to evaluate the Kabachnik parameters σ_I^P for a variety of amino-substituents at phosphorus.[12]

3. INTERACTION OF AZIDES WITH PHOSPHORUS OF VARIOUS COORDINATIONS AND VALENCIES

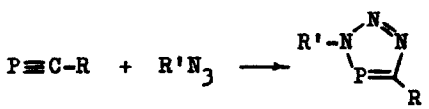
3.1. *One-coordinate phosphorus*

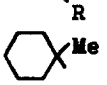
Imination of phospha-alkyne-azides does not proceed. Instead, the regiospecific cycloaddition of the azide takes place giving triazaphospholes (eqn 13) (for review, see ref. 117).

Table 4. Substituent σ_I values determined by eqn (12b)

Entry	Substituent	σ_I	Ref.
1	$-OC_8H_{17}$-n	0.28	*
2	$-OC_{12}H_{25}$-n	0.28	*
3	$-OCH_2CF_2CF_2H$	0.38 ± 0.02	*
4	$-OCH{=}CH_2$	0.43	15
5	$-OC(Ph){=}CH_2$	0.46 ± 0.02	15
6	$-OC(P(O)(OEt)_2){=}CH_2$	0.50	15
7	$-OCH{=}CHP(O)(OEt)_2$	0.47	15
8	$-OC(Me){=}CHCOOEt$	0.49	15
9	$-OC(CF_3){=}CHCOOEt$	0.53	*
10	$-OC(CH_2Cl){=}CHCl$	0.50	15
11	$-OC(Ph){=}CHCl$	0.54 ± 0.01	15
12	$-OC(Bu\text{-}t){=}CHCl$	0.51 ± 0.02	15
13	$-OCH{=}CCl_2$	0.50 ± 0.01	15
14	$-OC(Me){=}CCl_2$	0.52 ± 0.01	15
15	$-OC(Ph){=}CCl_2$	0.54 ± 0.02	15
16	$-OC(Bu\text{-}t){=}CCl_2$	0.51 ± 0.04	15
17	$-OC(Me){=}C(COOEt)_2$	0.51	15
18	$-OCH_2CH_2O-$	0.76 ± 0.02	36
19	$-OCH(Me)CH_2O-$	0.77 ± 0.02	36
20	$-OCH(Me)CH(Me)O-$	0.75	36
21	$-OC(Me)_2C(Me)_2O-$	0.65 ± 0.01	36
22		0.11	88
23	$-N(Me)COPh$	0.48	*
24		0.44	*
25		0.48	*
26	$-N(Ph)N{=}CMe_2$	0.31 ± 0.02	116
27		0.18	*
28	$-P(S)(OEt)_2$	0.35	21

* Our unpublished results.



R = Me[118], t-BuCH$_2$[119],  119,  119, i-Pr[119], t-Bu[120-122], 1-Ad[123]; (13)

R' = H, Me, CH_2CN, CH_2Ph, CH_2SiMe_3, t-Bu, $HC{=}CH_2$, Ph, 1-$C_{10}H_7$

The simplest representative, phosphaethyne, reacts with cyanogen azide in the gaseous phase exchanging its hydrogen atom for a cyano group.[124]

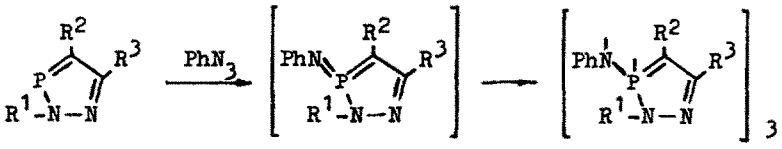
$$P{\equiv}CH + N_3CN \xrightarrow{\Delta} P{\equiv}C{-}CN \qquad (14)$$

3.2. *Two-coordinate phosphorus*

3.2.1. *Phospha-alkenes.* Phospha-alkenes couple with organic azides either by the Staudinger or by the [2+3]cycloaddition reaction (see reviews[125,126]). The oxidative imination leading to three-coordinate iminophosphoranes is illustrated in Schemes 2 and 3.

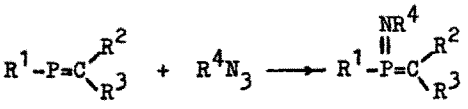
Formation of the cyclic product **80** in the reaction of the phosphaethylene **79** with phenyl azide (Scheme 4)[132] is indicative of a phosphazide intermediate.

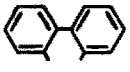
Compounds **81** (Scheme 5)[133,134] are believed to react with azides by a similar mechanism. The intermediate cycloadduct **82** decomposes giving imines **83** and the oligomeric cyclophosphines.[135]



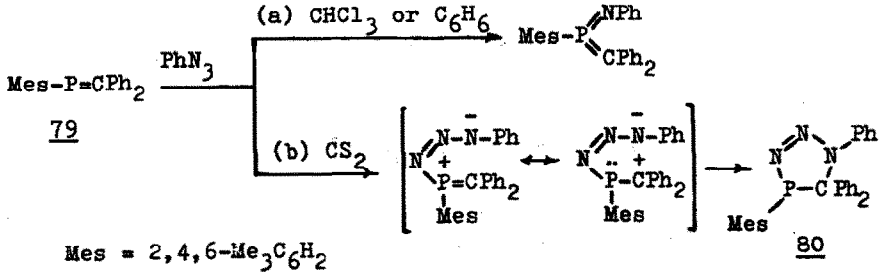
R^1	R^2	R^3	Ref.	Cyclic trimer
Ph	H	Me	127	
Ac	H	Me	127	
c.-C_6H_{11}	$(CH_2)_4$		128	

Scheme 2.



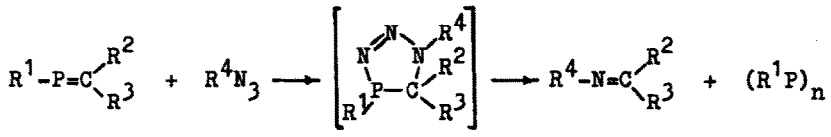
R^1	R^2	R^3	R^4	Refs
$(Me_3Si)_2N$	H	Me_3Si	Me_3Si	81,129
$(Me_3Si)_2N$	H	Me_3Si	$(Me_3Si)_2N(t\text{-}Bu)B$	64
2,4,6-$Me_3C_6H_2$	Me_3Si	Me_3Si	Me_3Si	129,130
2,6-$Me_2C_6H_3$			Ph	131

Scheme 3.



Mes = 2,4,6-$Me_3C_6H_2$

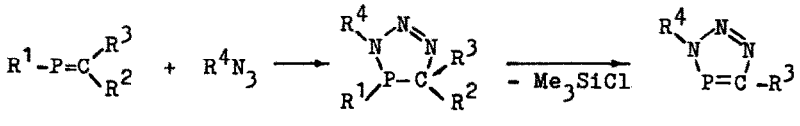
Scheme 4.



81 82 83

R^1	R^2	R^3	R^4	Ref.
Me_3Si	Me_3SiO	t-Bu	Me, Ph, $NCCH_2$	133
Ph	H	Me_2N	$PhCH_2$	134
Ph	Me	Me_2N	Ph	134

Scheme 5.



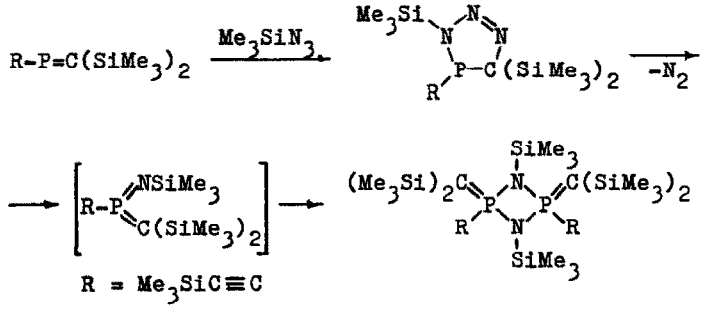
84 85

R^1	R^2	R^3	R^4	Ref.
Cl	Me_3Si	Me_3Si	Ph, $PhCH_2$	136
Cl	Me_3Si	Ph	Me, $NCCH_2$, $PhCH_2$, $EtOOCCH_2$, Ph	137
Mes	Ph	Ph	Tos	132

Scheme 6.

Scheme 6 illustrates the regiospecific 1,3-dipolar cycloaddition of phospha-alkenes with azides.[132,136,137] The orientation of the azide fragment in the cycloadduct **84** is opposite to that of the Staudinger product **80** (Scheme 4b). Elimination of trimethylchlorosilane from triazaphospholes **84** (R^1 = Cl, R^2 = Me_3Si) leads to novel heterocyclic products **85** containing a two-coordinate phosphorus atom.[136,137]

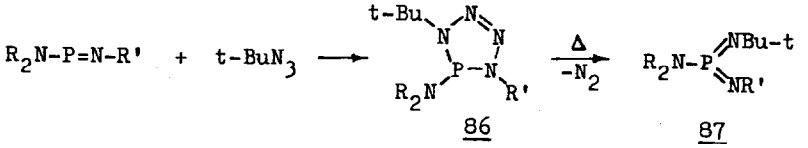
The product of 1,3-dipolar cycloaddition can eliminate nitrogen to give, finally, diazadiphosphetidine.[138]



(15)

3.2.2. *Phosphazenes and diphosphenes.* The interaction between azides and two-coordinate phosphorus compounds bearing P=N bond proceeds through a [2+3]cycloaddition step (see reviews[139,140]). The resultant cycloadduct **86** (eqn 16) decomposes with nitrogen elimination to give

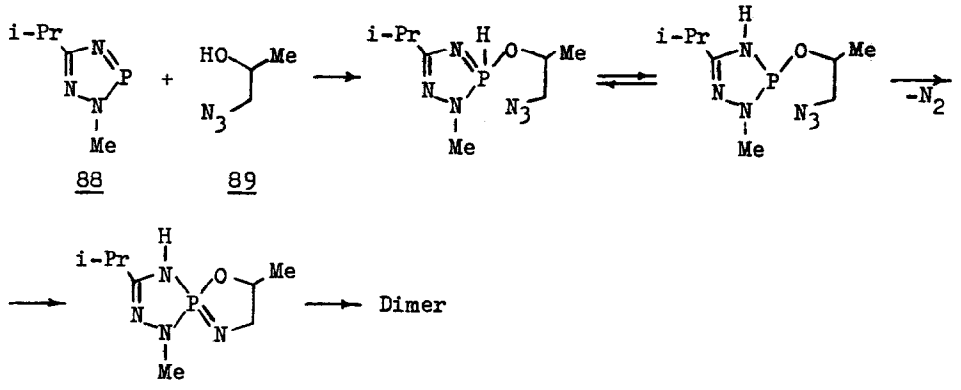
diiminophosphorane **87** identical with a Staudinger product.[141,142] However, there is no evidence for the Staudinger imination of the phosphazenes. They are also absent for other systems[64,143] where only end products of the type **87** were isolated and identified.



(16)

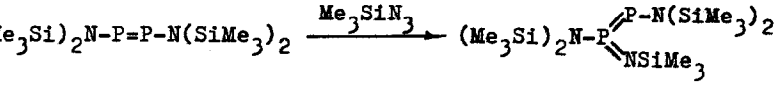
R = i-Pr, Me_3Si; R' = t-Bu, Me_3Si

The two-coordinate phosphorus atom in the triazaphosphole **88** reacts with the hydroxyl group but not the azido group of the azidoalcohol **89**.[144]



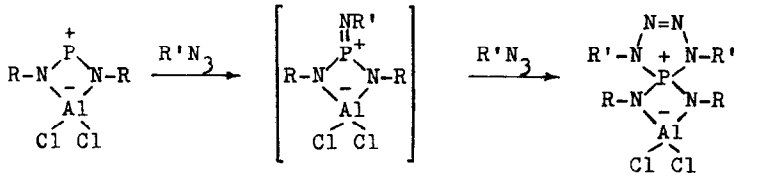
(17)

The only example of a reaction between an azide and a compound having P=P bound two-coordinate phosphorus was briefly reported without any comments on the reaction mechanism.[145]



(18)

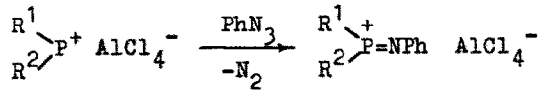
3.2.3. *Phosphenium ions.* Phosphenium ions have been recently intensively studied (for review see ref. 146): they are smoothly and quantitatively iminated with azides. The betaine **90** (eqn 19)[147,148] was the first such representative investigated in this reaction. It reacts with two equivalents of an azide, the second molecule $R'N_3$ being added across P=N bond of the intermediate imine **91** giving a spiroheterocycle **92**.



(19)

R = Me_3Si, R' = t-Bu, Et

The cations **93** react with one equivalent of an azide yielding the iminophosphonium cations **94** (Scheme 7).



93 94

R^1	R^2	Ref.
Me_2N	Me_2N	149
Et_2N	Et_2N	150
$MeNCH_2CH_2NMe$		150
$PhNCH_2CH_2NPh$		150
Me_2N, i-Pr_2N	Cl	151

Scheme 7.

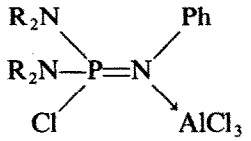
The reaction of chlorophosphenium ions with trimethylsilyl azide (Scheme 8)[152] is more complex because an exchange process precedes the imination.

The high reactivity of phosphenium ions toward azides is somewhat unexpected because in its classical form the Staudinger reaction is initiated by azide electrophilic attack on phosphorus. However, it is probable that the formally vacant 3p orbital on the P^+ site, as well as its known 'amphoterism' in reactions with Lewis acids and bases, promotes nucleophilic attack of azides at electrophilic phosphorus. In line with this suggestion, kinetic studies[153] of the reaction between $(Et_2N)_2P^+AlCl_4^-$ and substituted phenyl azides (CH_2Cl_2 solution, 7°C) shows that the electron-withdrawing substituents in the azides considerably reduce the reaction rate as evidenced by the linear Hammett relationship

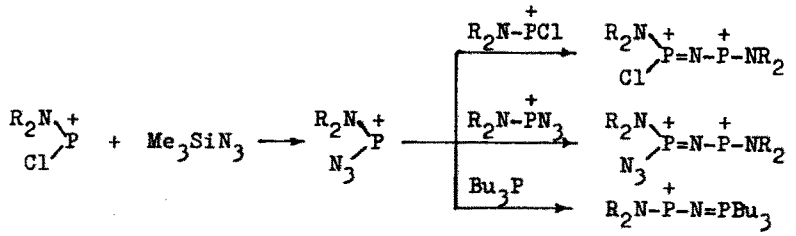
$$\log k_1 = -2.22\sigma - 1.26 \tag{20}$$

Furthermore, the kinetic results[153] suggest a reactive intermediate formation, presumably of the phosphazide type.

The recent communication[154] will encourage the revision of mechanistic opinion regarding phosphenium ion iminations. N. Burford *et al.*[154] have convincingly shown that the end product of the reaction between $(R_2N)_2P^+AlCl_4^-$ (R = Et, i-Pr) and PhN_3 is a Lewis acid–base complex **95** with a covalent P–Cl bond. This contrasts with the conventional view-point (Scheme 7).



95

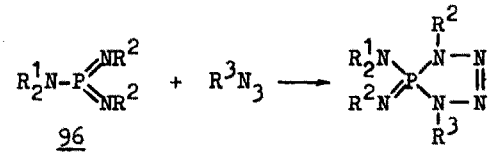


R = i-Pr; a counter-ion is $AlCl_4^-$

Scheme 8.

3.3. *High-valent three-coordinate phosphorus*

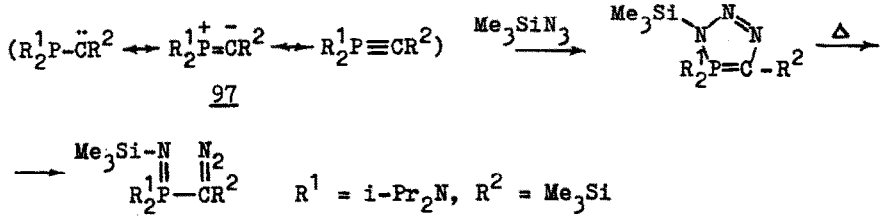
Such compounds react with azides by the [2+3]cycloaddition mechanism with a multiple P–N or P–C bond participation. The corresponding examples for the betaine **91** and diimides **96** are shown in equations 19 and 21,[142] respectively.



(21)

R^1 = i-Pr, Me_3Si; R^2 = t-Bu, Me_3Si; R^3 = Et, t-Bu

The reaction of λ^3-phosphinocarbene **97** with trimethylsilyl azide also proceeds in a similar fashion.[155]

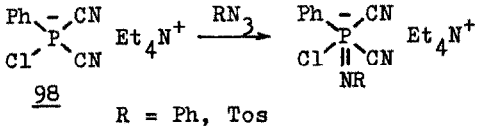


(22)

R^1 = i-Pr_2N, R^2 = Me_3Si

3.4. *Four- and five-coordinate phosphorus*

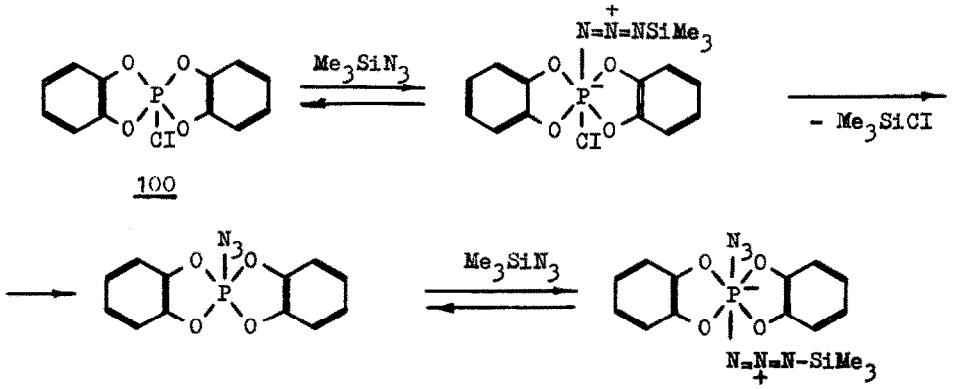
Among phosphorus compounds bearing P atom in coordination higher than 3, the imination with azides has been observed only for the phosphoranide **98**.[156]



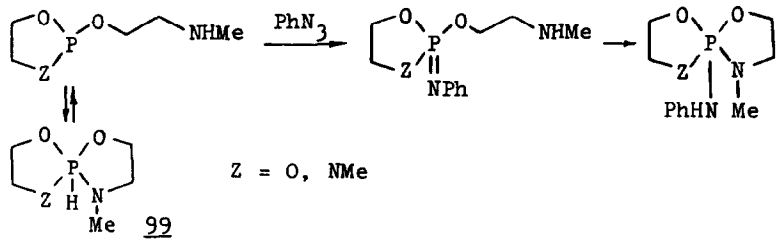
(23)

R = Ph, Tos

The phosphoranes **99** undergo ring opening on imination (Scheme 9).[157,158] However, if the rings are stable, as in the case of bis(*o*-phenylene)-chlorophosphorane **100**, the displacement reaction occurs at a pentacoordinate phosphorus atom through a hexacoordinate intermediate (eqn 24).[159]



(24)



99

Scheme 9.

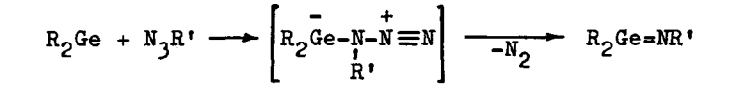
4. IMINATION OF ORGANO-ELEMENT COMPOUNDS WITH AZIDES

Besides phosphorus other elements from Groups IV, V, and VI undergo oxidative imination with azides. However, the mechanism of such transformations in most cases was not investigated, so their attribution to the Staudinger-type process is formal.

4.1. *Group IV elements. Germanium and tin*

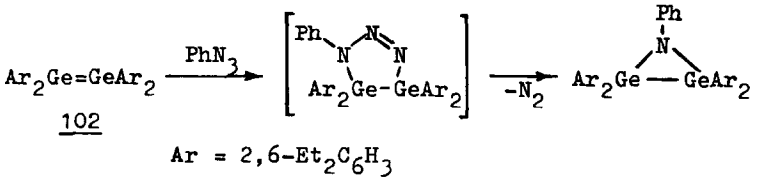
Only two-coordinate germanium and tin derivatives are iminated with azides. Germylene **101** reacts with azides giving iminogermanes (Scheme 10a) or products of RN_3 1,2-addition (Scheme 10b) and [2+3]cycloaddition (Scheme 10c) to the intermediate iminogermanes.[160]

In contrast with the classical Staudinger mechanism, nucleophilic attack of the azide at the Ge atom has been proposed[161] (eqn 25). However, this assumption was based exclusively on qualitative estimates of germylene reactivity.[162]



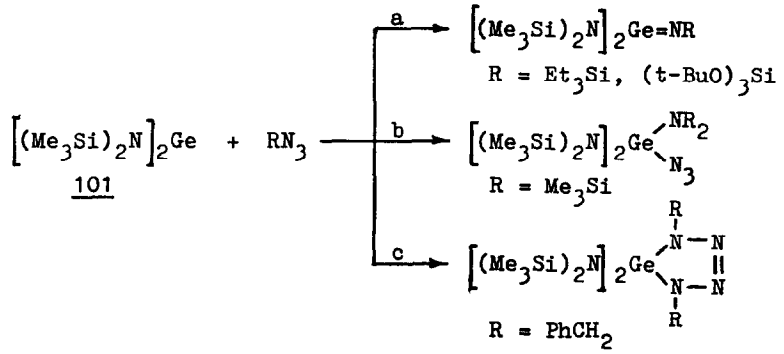
(25)

Digermene **102** adds to phenyl azide giving a cyclic product.[163]



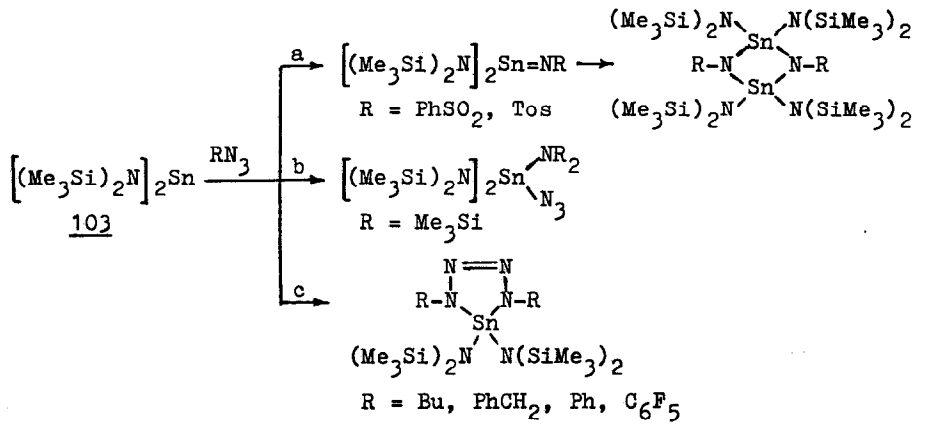
102

(26)



101

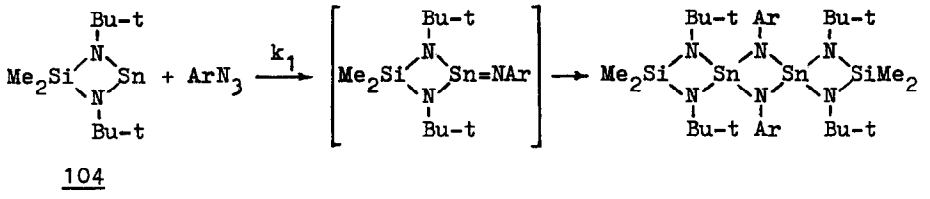
Scheme 10.



Scheme 11.

Stannylene **103**, a Group IVA analogue of germylene **101**, reacts with azides similarly. Scheme 11 includes the dimerization of the intermediate stannylimines (route **a**)[164] or their addition to azides (routes **b**[164] and **c**[165]).

The study of stannetidine **104** imination with aryl azides (eqn 27)[166] has revealed that tin, like tervalent phosphorus in the Staudinger reaction, is nucleophilic.[167]

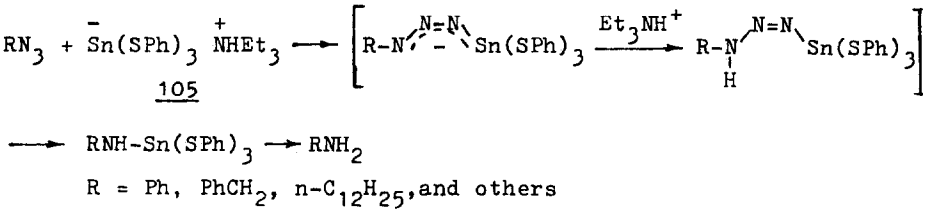


(27)

The second order rate constants k_1 for the reaction (eqn 27) ($AcNMe_2$ solvent, 25°C) correlate with σ^0 values of the substituents in phenyl azides by the Hammett equation (eqn 28).[167]

$$\log k_1 = 2.38\sigma^0 - 1.56 \tag{28}$$

A phosphazide-like intermediate has been postulated in the reduction of azides to amines by a tin reagent **105**.[168]

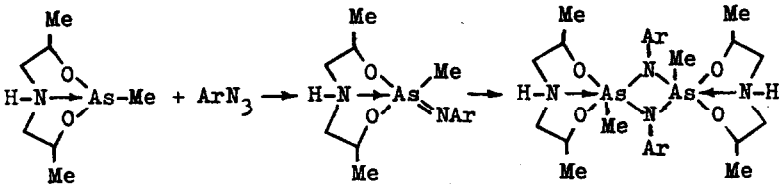


(29)

4.2. *Group V elements. Arsenic, antimony, tantalum, and vanadium*

The possibility of imination of phosphorus nearest analogues from Group V, i.e. arsenic and antimony, with organic azides, was considered as early as 1919 by Staudinger and Meyer.[2] However, very few investigations, especially with arsenic derivatives, have been done since then.

Equation 30[169] illustrates the rare example of a facile imination of arsenic whose reactivity is enhanced by transannular interaction in the heterocycle **106**.

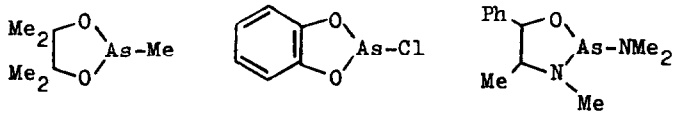


(30)

106 **107**

Ar = 2,4,6-$(NO_2)_3C_6H_2$, Tos

The end product is the imine dimer **107**. Picryl azide also iminates arsenic in the heterocycles **108–110**. It was presumed that the reaction proceeds through an intermediate charge-transfer complex formed by the azide and the arsenic compound.[169]



108 **109** **110**

Triaryl-[170] and trialkyl-stibines[171] are smoothly iminated with arenesulfonyl azides giving the corresponding stibinimines.

$$R_3Sb + ArSO_2N_3 \xrightarrow{k_1} R_3Sb{=}NSO_2Ar$$

$$R = Ph, Et, Pr;\ Ar = Ph, p\text{-}Tol, p\text{-}NO_2C_6H_4 \qquad (31)$$

Kinetic investigation[172] has shown that in the reaction of Ph_3Sb with substituted benzenesulfonyl azides, the latter acts as an electrophile thus providing close analogy with the classical Staudinger reaction. The corresponding second order rate constants (THF, 40°C) correlate with σ^n parameters for substituents in the azides according to equation 32.

$$\log k_1 = 1.53\sigma^n - 2.79 \qquad (32)$$

Some examples of azide imination are known for tantalum in its complexes [173] and for vanadium in decamethylvanadocene **111**[174–176] (e.g. eqn 33).[175]

$$\underset{\mathbf{111}}{Cp^*_2V} + PhN_3 \longrightarrow Cp^*_2VN_3Ph \longrightarrow \underset{\mathbf{112}}{Cp^*_2V{\equiv}NPh} \qquad (33)$$

$Cp^* = \eta\text{-}C_5Me_5$

In the last case, the isotopic tracer ^{15}N is completely transferred from the labeled azide $N_2{}^{15}NPh$ into the imine **112**.[176]

4.3. *Group VI elements*

In recent years, the reactions of Group VI element derivatives with organic azides has attracted more and more attention in view of their potential synthetic utility. There were many reports on imination of sulfur in halogenothiophenes,[177] sulfides,[178–180] and sulfoxides.[181–183] The process outlined in equation 34 was proposed as a convenient method for the preparation of sulfilimines.[180]

$$R_2S + TosN_3 \xrightarrow{\Delta,\ \text{Copper catalyst}} R_2S{=}NTos \qquad (34)$$

$$R = Bu,\ PhCH_2,\ Ph$$

In most cases the reaction mechanism was presumed to involve intermediate nitrene species resulting from azide thermolysis.

The Staudinger-like reaction of diisobutyl telluride with tosyl azide was utilized for the synthesis of N-tosylimines **113** via aza-Wittig conversion of intermediate tellurilimines.[184]

$$\text{i-Bu}_2\text{Te} \xrightarrow{\text{TosN}_3} [\text{i-Bu}_2\text{Te}{=}\text{NTos}] \xrightarrow{\text{ArCHO}} \underset{\mathbf{113}}{\text{ArCH}{=}\text{NTos}} + \text{i-Bu}_2\text{TeO} \qquad (35)$$

$$\text{Ar} = \text{XC}_6\text{H}_4(\text{X} = \text{H, 2-MeO, 4-MeO, 4-Cl, 4-NO}_2)$$

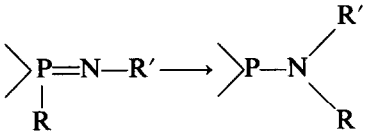
The oxidative imination of Mo(II)[185] and Mo(IV),[186–188] W(II) and W(IV)[185] or U(III)[189,190] derivatives with organic azides is widely used to prepare imido-complexes of the metals.

5. REARRANGEMENTS OF IMINOPHOSPHORANES

The structure of iminophosphoranes is characterized by a relatively high lability that is exhibited in a variety of rearrangements discussed in this section.

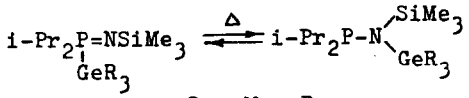
5.1. *Imide–amide rearrangements*

5.1.1. 1,2-*Migrations*. These rearrangements are described by the following general equation



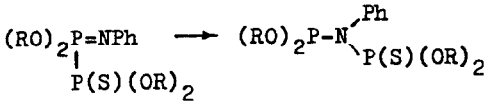
(36)

The 1,2-shift of an organo-element group from phosphorus to imine nitrogen results in a reduction of a phosphorus coordination. In equations 37–39 some examples of germanium,[191] phosphorus,[192] and silicon[193] 1,2-migrations are presented.



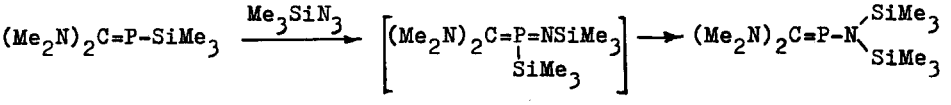
(37)

R = Me, Bu



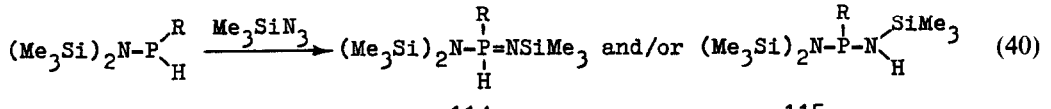
(38)

R = Et, Pr



(39)

There were many reports on the imination of secondary phosphines which are accompanied by a formal 1,2-hydrogen migration[28,194–196] (e.g. eqn 40[194]).



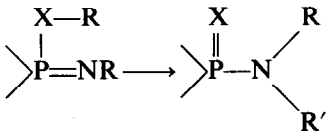
(40)

114 115

R = t-Bu, i-Pr

The products **114** and **115** do not inter-convert. It was, therefore, supposed that they are formed via independent routes in the course of nitrogen elimination from a common phosphazide intermediate.

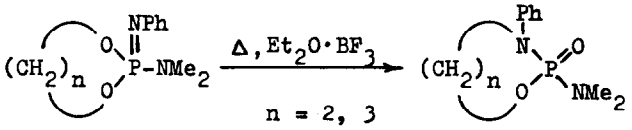
5.1.2. 1,3-*Migrations*. The title rearrangements proceed in a fashion outlined in equation 41. They were discussed in detail earlier.[197] In this section new data are surveyed.



(41)

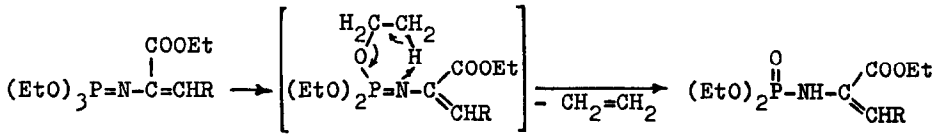
X = O, S

The alkyl migration in the triad O–P–N,[21,46,198–202] which is typical of such rearrangements, was also observed in cyclic systems in the presence of a catalyst ($Et_2O \cdot BF_3$) (eqn 42)[203] and without one.[33]



(42)

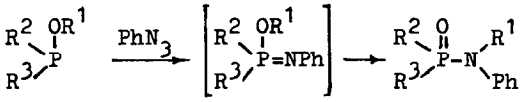
In the case presented in equation 43 the migration is complicated by the elimination of ethylene.[204]



(43)

R = Me, Et, Pr, Ph

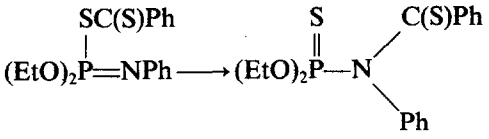
In this type of rearrangement alkenyl, acyl, benzimidoyl, thiophosphoryl, and trimethylsilyl groups can also participate (Scheme 12).



R^1	R^2	R^3	Refs
$C(CF_3)=CHCOOEt$	EtO	EtO	205,206
$C(O)CF_3$	$-OCH_2CH_2O-$		207
C(Ph)=NMe	EtO	EtO	208
$P(S)(OEt)_2$	EtO	EtO	199
Me_3Si	Me	Me	209

Scheme 12.

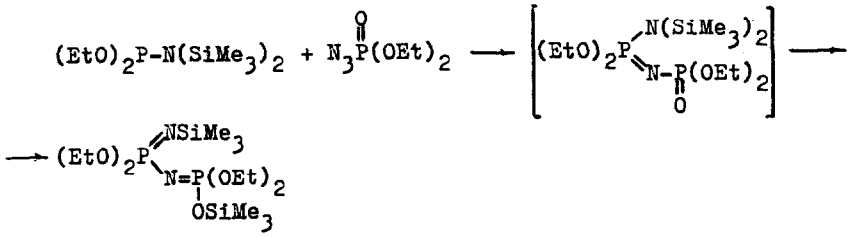
A similar migration was also observed in a triad S–P–N.[210]



(44)

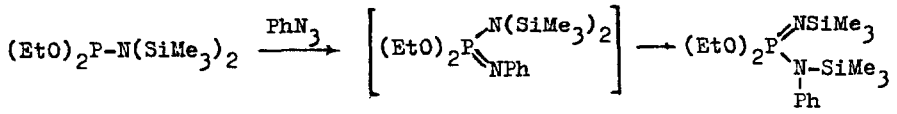
5.2. *Imide–imide rearrangements*

Some new examples of the known rearrangement[197] were published. Trimethylsilyl 1,5-shift from nitrogen to oxygen atom in a N–P=N–P=O system is accompanied by displacement of double bonds to give a new iminophosphorane.[55]

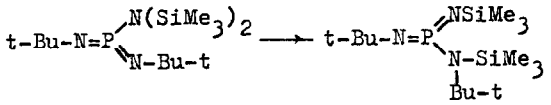


(45)

The migrations in a N–P–N triad shown in equations 46[55] and 47[142] can also be attributed to the imide–imide rearrangement.



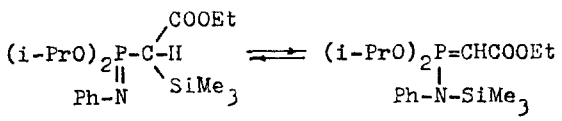
(46)



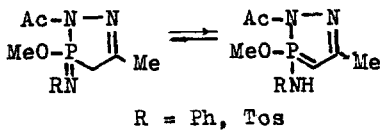
(47)

5.3. *Imide–ylide rearrangements*

These rearrangements occur in a C–P–N triad and are known in a silylotropic (eqn 48)[211] or prototropic version (eqn 49).[39,40]



(48)

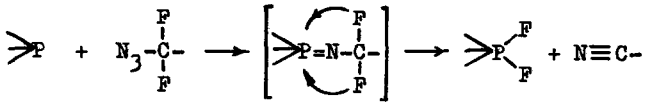


R = Ph, Tos

(49)

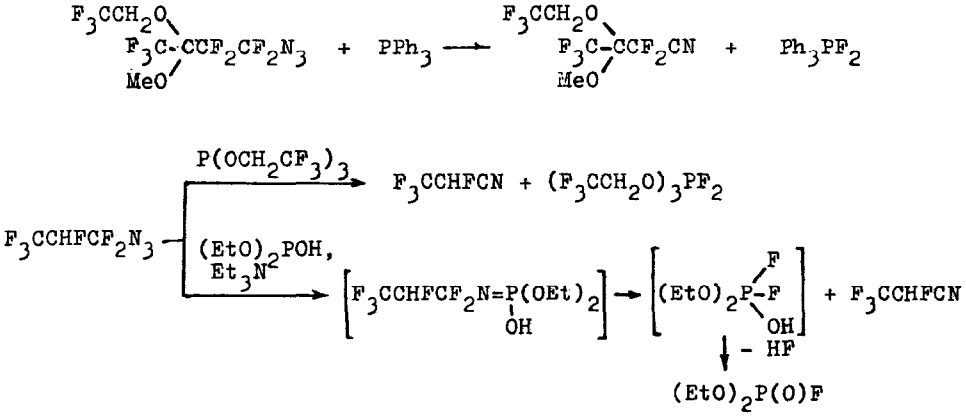
5.4. *Imide–phosphorane rearrangement*

This rearrangement accompanies the Staudinger imination with 1,1-difluoroalkyl azides. The 1,3-migration of active fluorine atoms in an iminiphosphorane leads to formation of energetically more favourable products, i.e. difluorophosphorane and nitrile.



(50)

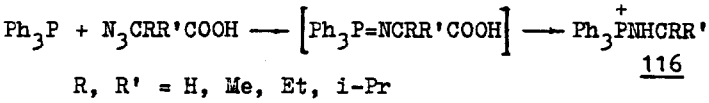
Scheme 13 illustrates the representative reactions with phosphines,[212] trialkyl phosphites,[213,214] and dialkyl phosphites.[215]



Scheme 13.

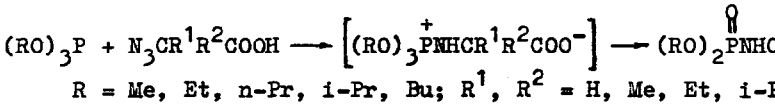
5.5. *Prototropic rearrangements*

The previously mentioned rearrangements involving imine nitrogen atom (eqn 49) are especially characteristic of iminophosphoranes derived from azidocarboxylic acids.[202,216,217] Migration of a carboxylic proton to a P=N nitrogen atom leads to the betaine **116** (eqn 51).[202,217] In the presence of alkoxyl groups at phosphorus, the intermediate betaines rearrange into amidophosphates (eqn 52).[202,216,217]



(51)

R, R' = H, Me, Et, i-Pr



(52)

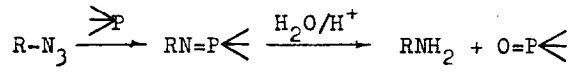
R = Me, Et, n-Pr, i-Pr, Bu; R^1, R^2 = H, Me, Et, i-Pr

There were also reports on 1,3-proton shifts in iminophosphorane. Alkenyl substituents at the phosphorus[218] or the nitrogen atom[219] do not affect P=N bond.

6. REACTIONS OF IMINOPHOSPHORANES

6.1. *Hydrolysis*

6.1.1. *Synthesis of amines.* Hydrolysis of the Staudinger iminophosphorane products is a convenient method for the synthesis of amines (see reviews[183,220]).



(53)

Triphenylphosphine is routinely employed as the phosphorus reagent, and the resultant phosphinimine is hydrolyzed with water, sometimes with diluted acids or ammonia. This method is characterized by high chemo- and stereo-selectivity. The reduction of N_3 group in an azide does not affect other functional groups. It is widely used in the synthesis of biologically active amines, including derivatives of spermine, spermidine[221] and mitosene.[222] Some representative examples of amines obtained in this way are depicted in Chart 7.

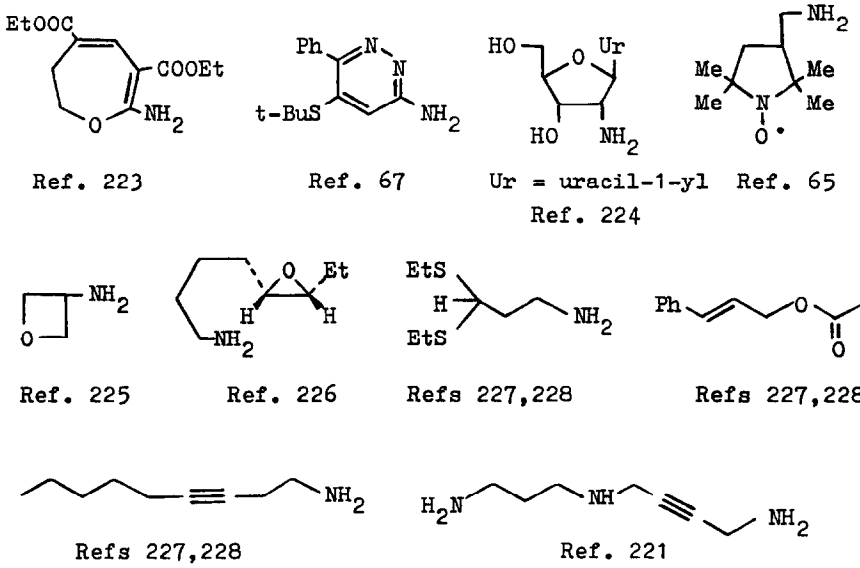
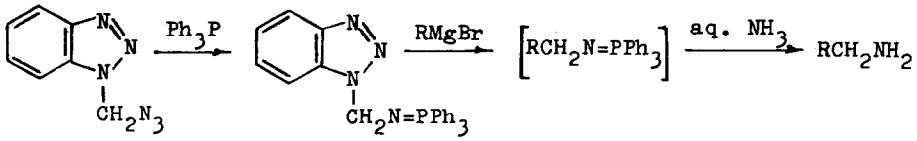


Chart 7.

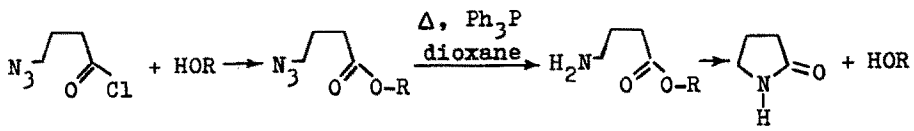
Benzotriazole **117** has been proposed as a synthon for the preparation of various amines[229] and their derivatives[230] by a one-carbon homologation of the original hydrocarbon moiety R in the Grignard reagent RMgBr.



(54)

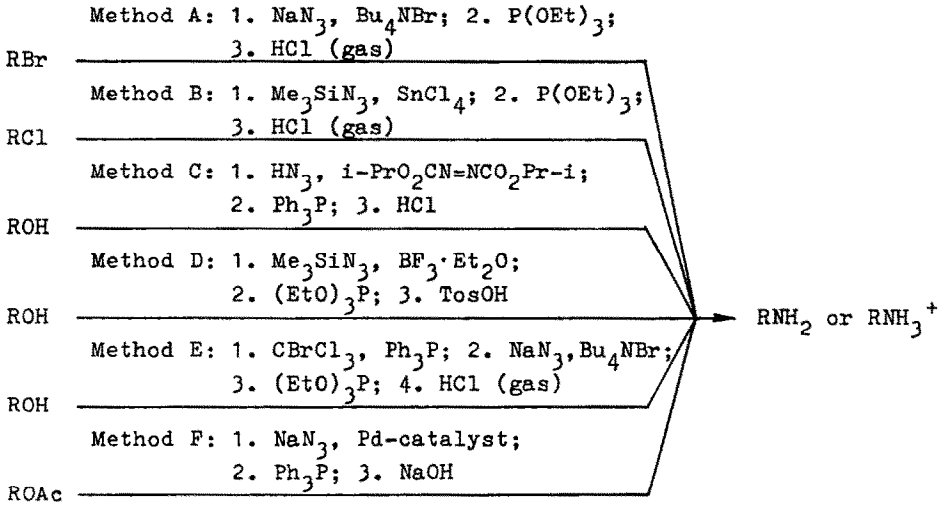
R = $PhCH_2$, $PhC{\equiv}C$, n-$C_{12}H_{25}$, 2-thienyl, 1-$C_{10}H_7$

The reduction of azides to amines has been employed as a means for selective removal of groups protecting hydroxyl functions in complex carbohydrates and other polyhydroxylated natural products.[231]



(55)

A number of simple one-pot approaches for the synthesis of amines from primary and secondary alkyl bromides,[232,233] tertiary alkyl chlorides,[234] alcohols[235-237] or acetates[238] have been developed. These reagents, without isolation of intermediate products, are converted into azides then condensed with triethylphosphite or triphenylphosphine and, finally, hydrolyzed. Details of the method are given in Scheme 14 and in Table 5 where some examples are listed.

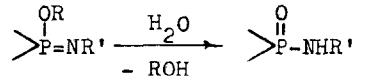


Scheme 14.

Table 5. One-pot synthesis of amines RNH_2 from RX

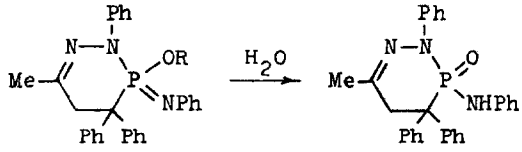
R	X	Method in Scheme (14)	Yield of RNH_2 or RNH_3^+, %	Ref.
$PhCH{=}CHCH_2$	Br	A	60	232
$HC{\equiv}CCH_2$	Br	A	80	232
s-Bu	Br	A	64.5	232
c.-C_5H_9	Br	A	79	232
EtOOC(Me)CH	Br	A	68	232
t-Bu	Cl	B	46	234
$Me_2(PhCH_2)C$	Cl	B	36	234
(R)-$Me(CH_2)_5CHMe$	HO	C	58	235
$Me_2(Et)C$	HO	D	54	236
$PhCH_2$	HO	E	78	237
n-Bu(Et)CH	HO	E	67.5	237
$Me_2C{=}CHCH_2$	AcO	F	61	238
$Me_2C{=}CH(CH_2)_2C(Me){=}CHCH_2$	AcO	F	59	238

6.1.2. *Synthesis of phosphorus acid amides.* Aqueous hydrolysis of iminophosphoranes under mild conditions proceeds via an Arbuzov rearrangement which provides *N*-substituted phosphorus acid amides.[29,54,239–241]



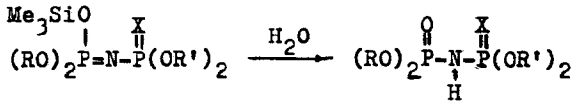
(56)

Equations 57,[29] 58,[54] and 59[240,241] illustrate this synthetic strategy.



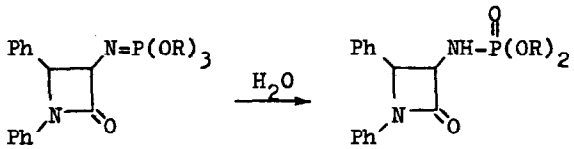
(57)

R = Me, Et



(58)

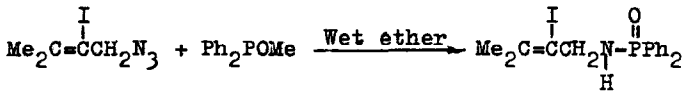
R, R' = Me, Et, Bu; X = O, S



(59)

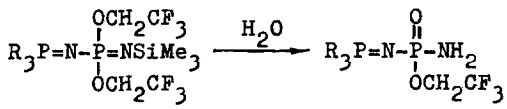
R = Me, Et, Pr, Ph

Phosphorus acid amides are the end products of the Staudinger reaction when it is carried out in a wet medium (eqn 60).[242]



(60)

N-Trimethylsilyliminophosphoranes **118**, on hydrolysis, give amides **119** possessing unsubstituted amino groups.[243]

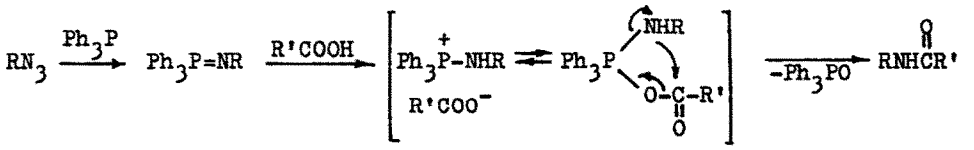


(61)

118 **119**

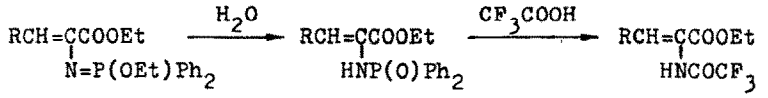
R = Me, Me_2N

For *N*-alkylamidophosphates, a one-pot synthesis similar to those presented in Scheme 14 has been developed starting from tertiary alcohols[236] or alkyl bromides[244] and triethyl phosphite.



Scheme 15.

Mild hydrolysis of iminophosphoranes is also used for phosphinyl protection of amino groups.[245]

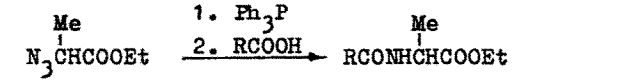


(62)

R = Me, Et, n-Pr, i-Pr, Ph

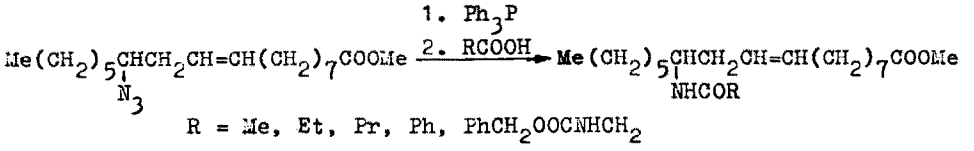
6.1.3. *Synthesis of carboxylic acid amides* (*acylamines*). The acidolysis of iminophosphoranes is a convenient procedure providing carboxylic acid amides with protected amido groups.[246]

Later on, triphenylphosphine in Scheme 15 was substituted for triethylphosphine, as Et_3PO is more easily separated from the reaction mixture than Ph_3PO.[247] This method was considered to be suitable for the preparation of small peptides (eqn 63),[248] peptido-lipids (eqn 64)[249] or acetamido-substituted glycopeptides.[250]



(63)

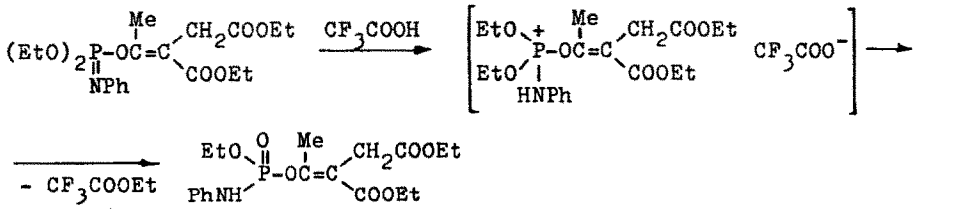
RCOOH = Boc-Gly-OH, Bz-Gly-OH, Z-Gly-OH, etc.



(64)

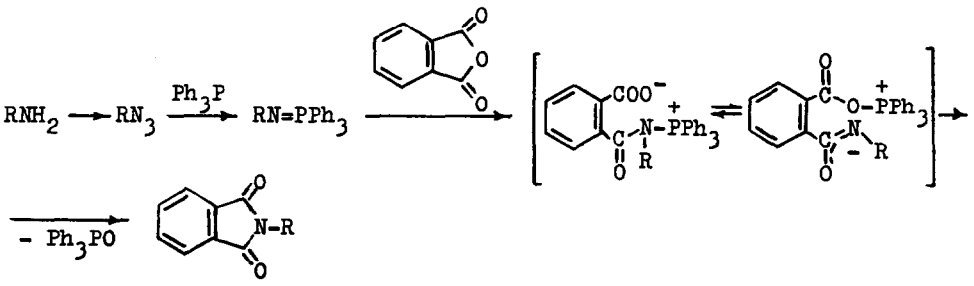
R = Me, Et, Pr, Ph, $PhCH_2OOCNHCH_2$

When an iminophosphorane has an alkoxyl substituent at phosphorus, the quasi-phosphonium salt formed on imine nitrogen protonation eliminates an alkyl group and is converted into the corresponding amidophosphate (eqn 65).[251]



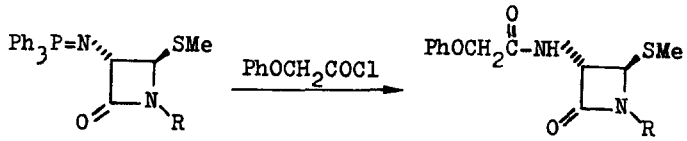
(65)

The mechanism, similar to that outlined in Scheme 15, also operates in the reaction between iminophosphoranes and phthalic anhydride.[252,253] Such a transformation may be adopted for amino group protection, particularly in derivatives of sugars, di- or oligosaccharides.[252]



(66)

Acylamines may also be prepared by treating iminophosphoranes with acyl chlorides[253-255] as in the synthesis of penicillin and cephalosporin derivatives[254,255] (eqn 67[254]).



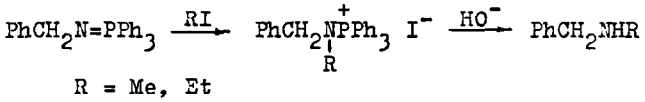
(67)

R = $Ph_2CHOOCCMe_2$, $HOOCCMe_2$

6.2. *Alkylation*

The alkylation of iminophosphoranes with alkyl halides is a typical reaction of such phosphorus compounds. It was comprehensively discussed in previous reviews.[197,220]

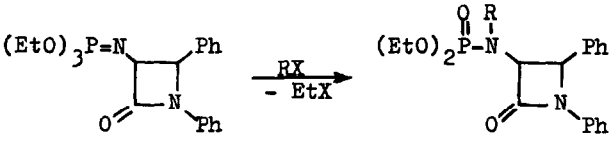
In the case of phosphinimines, the reaction is limited to addition of an alkyl group to imine nitrogen atom,[65,113,230,253,256] and occasionally to other, more nucleophilic sites.[223] Hydrolysis of the resultant phosphonium salts is used to obtain secondary amines (eqn 68).[230]



(68)

R = Me, Et

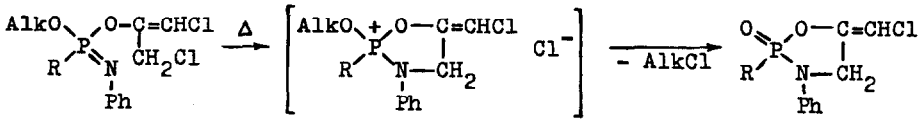
Imidophosphates and imidophosphonates eliminate alkyl halide after alkylation (acylation) and are transformed into the corresponding phosphorus acid amides[197,203,233] (eqn 69[241]).



(69)

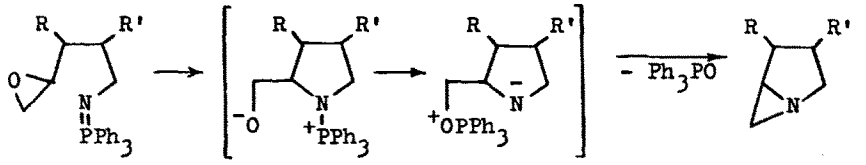
RX = MeI, AcBr

Interesting intramolecular variants of alkylation by participation of a carbon atom activated by a halogeno-substituent (eqn 70)[257,258] or an epoxy group (eqn 71)[259] have been proposed.



(70)

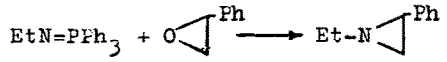
Alk = Me, Et; R = EtO, Et_2N



(71)

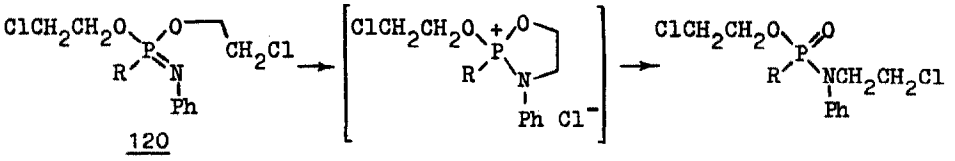
R = $PhCH_2$, R' = Me

The bimolecular reaction with epoxides yields aziridines.[230]



(72)

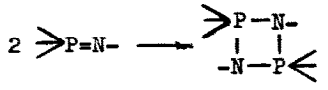
In contrast with equation 70, the cycle formed by the imine **120** on intramolecular alkylation is unstable and its cleavage results in an imide–amide rearrangement of the starting molecule.[229]



(73)

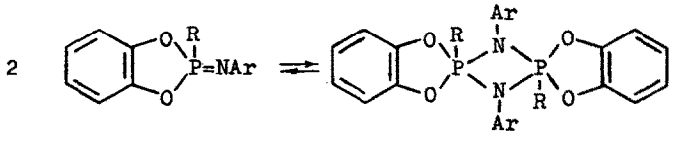
6.3. *Cyclization reactions*

6.3.1. *Cyclodimerization.* Cyclodimerization is one of the most typical features of iminophosphoranes.[3]



(74)

There are numerous reports on dimerization of cyclic[12,14,31–36,39,40,43,57,200–202,217,260,261] and acyclic[11,12,262] phosphorus imino derivatives. In the first case, the most pronounced driving force of the reaction is a decrease in a ring strain resulted by a spirophosphorane formation (eqn 75).[31,32]

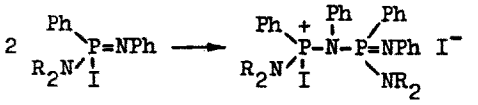


(75)

R = Hal, AlkO, Alk_2N, ArO

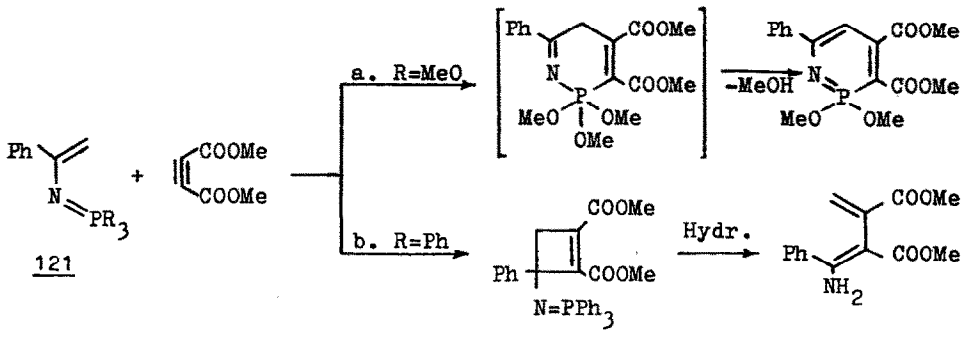
The cyclodimerization is controlled by a delicate balance of electronic (electrophilicity of phosphorus and nucleophilicity of nitrogen atom in P=N bond) and steric factors.[31,32]

For *P*-halogenated iminophosphoranes, the unusual acyclic dimerization has been reported[10,263] (eqn 76[10]).



(76)

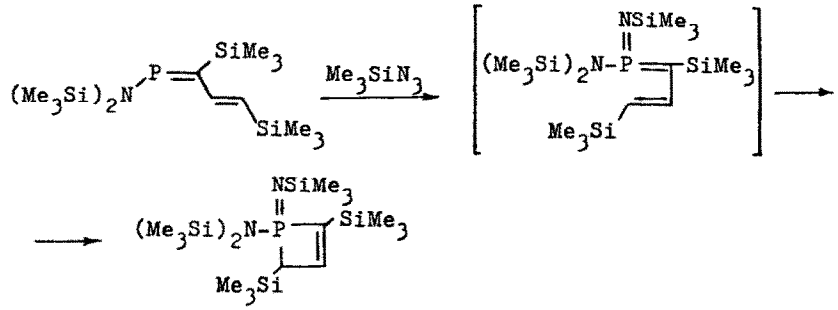
R = Et, Pr



Scheme 16.

6.3.2. *Cycloaddition to alkynes and alkenes.* This reaction is possible in the case of iminophosphoranes having an unsaturated C=C bond. *N*-Vinyliminophosphoranes **121** can participate in Diels–Alder [2+4]cycloaddition with dimethyl acetylene-carboxylate as the diene (Scheme 16a) or in [2+2]cyclization as the ene component (Scheme 16b).[264] For additional examples see Section 6.4.

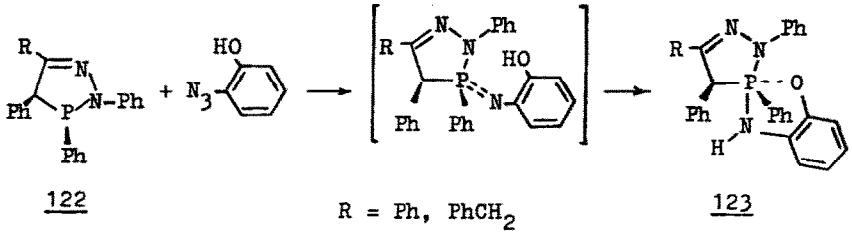
Equation 77 illustrates the intramolecular version of the cycloaddition reaction.[265]



(77)

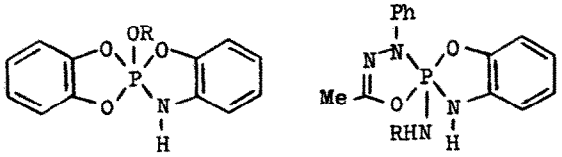
6.3.3. *Spirocyclization.* Spirocyclization has attracted much attention since the first publications by Cadogan.[266,267] The process includes the intramolecular 1,2-addition of an iminophosphorane reactive side group, H–X (X = O, COO, N), across the P=N bond resulting in a ring closure. Such reactions are the most characteristic of cyclic imines which thereby convert to less strained spirophosphoranes. Some examples classified according to the type of a H–X group are discussed below.

6.3.3.1. *Hydroxyl group participation.* The reaction of diazaphospholes **122** with *ortho*-azidophenol proceeds in a stereoselective manner and leads to spiroadducts **123** (eqn 78).[268] The intermediate iminophosphorane undergoes very rapid cyclization, so all attempts to detect it in the reaction mixture were unsuccessful.



(78)

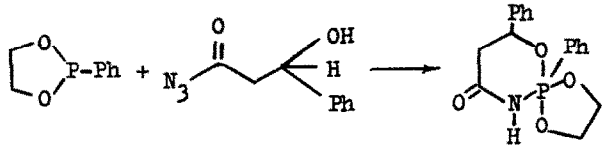
In a similar way, the spirophosphoranes **124**[269] and **125**[270] were prepared.



124 125

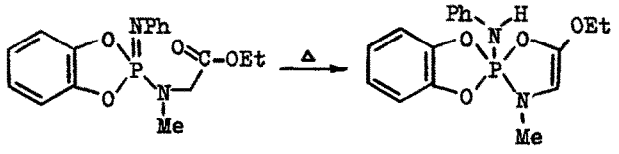
R = Me, Et R = Ph, c.-C_6H_{11}

Equation 79[271] exemplifies the participation of alcoholic hydroxyl in this reaction. The analogous cyclization was also observed on interaction between acyclic phosphites and 2-azidoalcohols.[272]



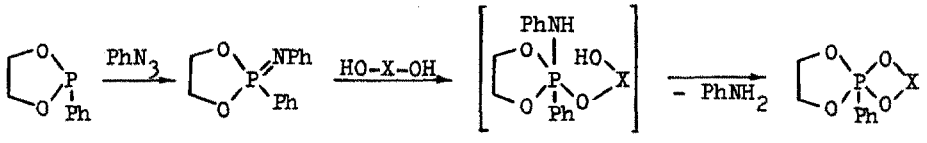
(79)

An interesting case of enolic hydroxyl participation in the spirocyclization has been reported.[260]



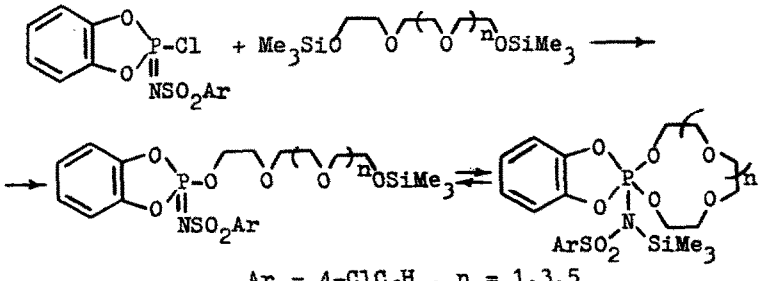
(80)

The reaction involving diol addition across the P=N bond and subsequent displacement of the amino group by the second hydroxyl was proposed as a simple one-pot approach to the synthesis of spirophosphoranes.[273]



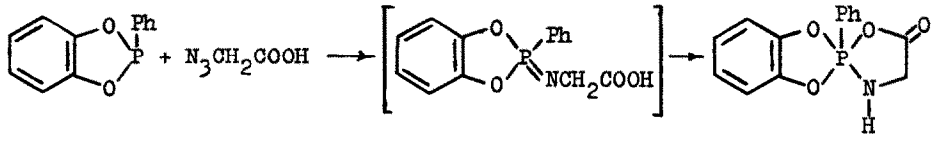
X = $(CH_2)_n$, n = 2-5 (81)

Equation 82[274] gives an example of a trimethylsilyloxy group participation in a spirocyclization which leads to phosphorus-containing crown ethers.



Ar = 4-ClC_6H_4, n = 1,3,5 (82)

6.3.3.2. *Carboxyl group participation.* A rare example of carboxyl participation in the spirocyclization is presented in eqn 83.[202,217]

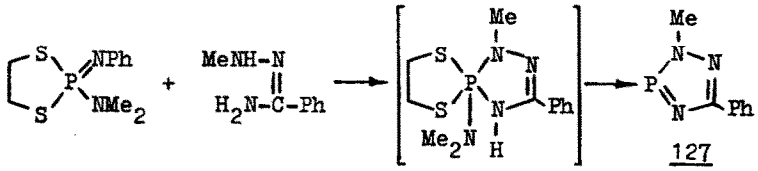


(83)

In the absence of cyclic substituents at phosphorus, the conversion of the intermediate imine stops at the stage of imine nitrogen protonation resulting in betaine formation (eqns 51 and 52).

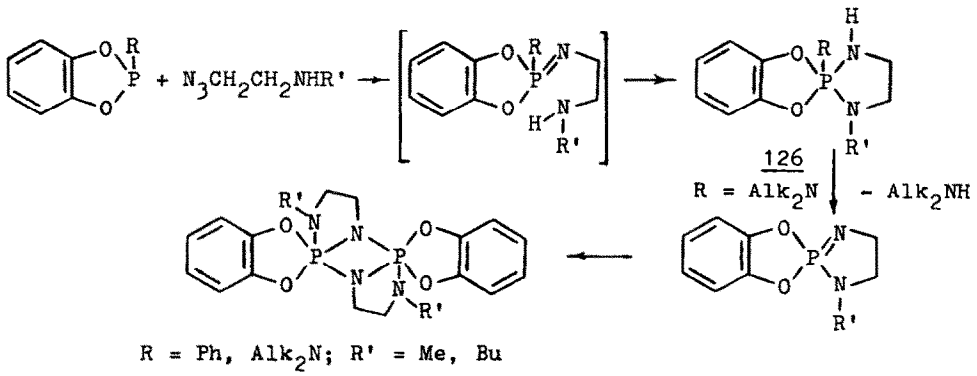
6.3.3.3. *Amino group participation.* The spirocyclization of this type has been observed in the reactions depicted in Scheme 17.[201,202] Amino groups (R = Et_2N, i-Pr_2N) attached to phosphorus in spirophosphorane **126** are eliminated on heating. Acyclic iminophosphoranes do not undergo such a cyclization.[200,201] It should be noted that the proton transfer to imine nitrogen preceding the spirocyclization occurs only from an amino group as shown in Scheme 17. An amidic proton does not migrate to the P=N bond so that the Staudinger reaction with azides $N_3CH_2CH_2NHCOR$ is not accompanied by spirocyclization.[200]

The intermolecular spirocyclization of an iminophosphorane with diamines has been reported (eqn 84).[275] The reaction proceeds via successive eliminations of exocyclic amino groups at phosphorus to give triazaphosphole **127** having a two-coordinate P atom.

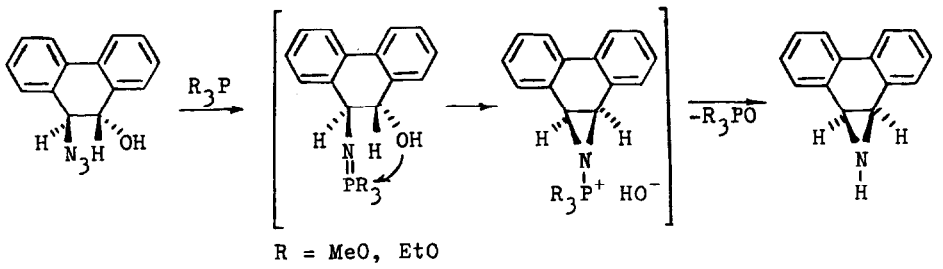


(84)

6.3.4. *Reductive cyclization.* Such a cyclization, characteristic of the Staudinger products derived from 2-azidoalcohols, gives aziridines. As an example, the reaction of 10-azido-9,10-dihydrophenanthren-9-ol with trialkyl phosphites[276,277] is shown in Scheme 18. This reaction has been employed in the synthesis of the arene imine **128**,[278] epimino ionone **129**,[279] the LTA_4 aza-analog **130**,[280] and the optically active aziridinecarboxylic acids **131**.[281]



Scheme 17.



Scheme 18.

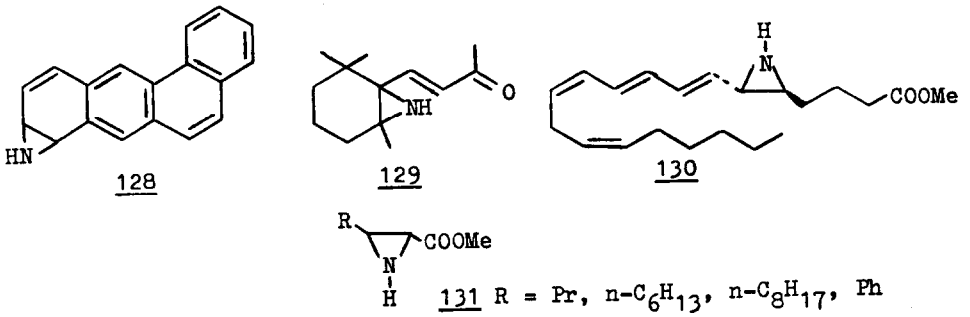


Chart 8.

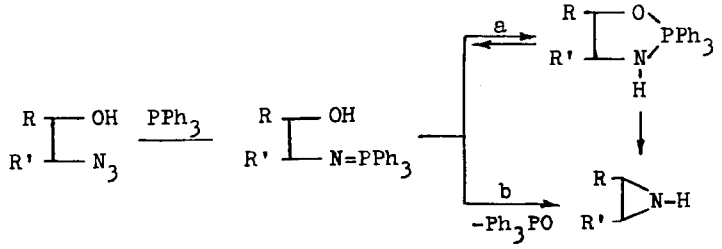
The mechanism of the reductive cyclization presumably includes the following competitive processes: the HO group intramolecular addition across P=N leading to oxazaphospholidines (Scheme 19a) and the nucleophilic attack of imine nitrogen at the carbon atom bound to hydroxy group resulting in aziridine cycle closure (Scheme 19b).[282]

It is possible that the azetidine in eqn 85 is also formed by a similar mechanism.[283]

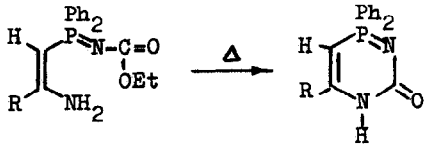
$$R_3P + N_3(CH_2)_3OH \longrightarrow R_3P{=}N(CH_2)_3OH \xrightarrow[-R_3PO]{\Delta} H{-}N\square \qquad (85)$$

R = Bu, Ph

6.3.5. *Other cyclization reactions.* In this section some additional transformations, which do not fit into categories described so far, are discussed. They include the intra- and inter-molecular cyclizations of iminophosphoranes with or without P=N bond participation. Among them, the condensation reactions involving alkoxycarbonyl and amino functions form a special group.[284–287] The amino group can pre-exist in a starting imine molecule (eqn 86)[284] or be generated by hydrolysis of P=N function before cyclization to lactams[286,287] (eqn 87)[287] or other products.[288]

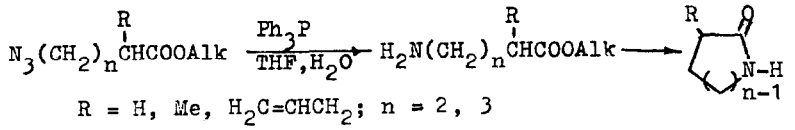


Scheme 19.



(86)

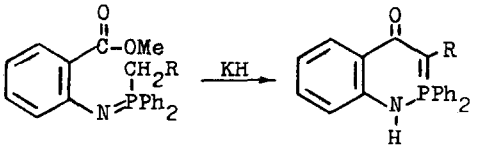
R = p-Tol, c.-C_6H_{11}



(87)

R = H, Me, H_2C=$CHCH_2$; n = 2, 3

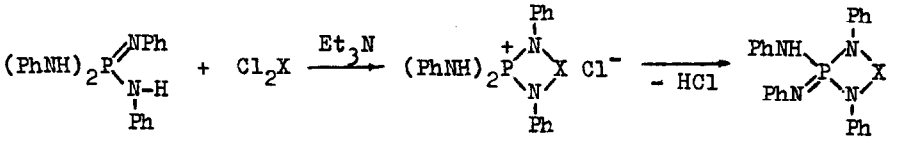
The nucleophilic substitution in a methoxycarbonyl group can also result in cyclization.[289]



(88)

R = Me, CH_2=CH, Ph

Recently, an interesting cyclization was observed[290,291] in the reaction of triamidoiminophosphate **132** with phosphorus or silicon dihalo-derivatives that involves two nitrogen atoms of the triad N–P–N in the starting imide (eqn 89[290]).

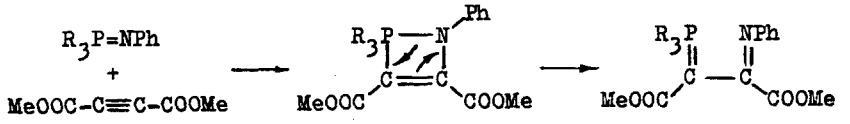


(89)

132 X = P-NMe_2, $SiMe_2$

6.4. *Insertion reactions*

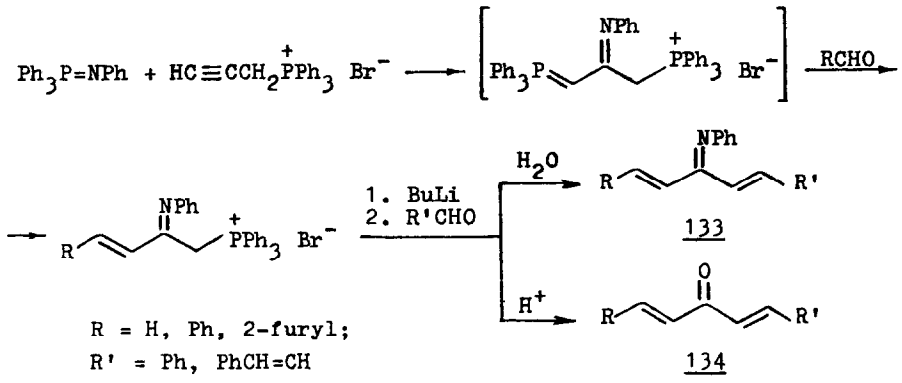
Insertion into the P=N bond of iminophosphoranes takes place upon their interaction with alkynes. It includes a [2+2]cycloaddition step and provides phosphorus ylides after redistribution of bonds in the four-membered intermediate cycle.[37,292]



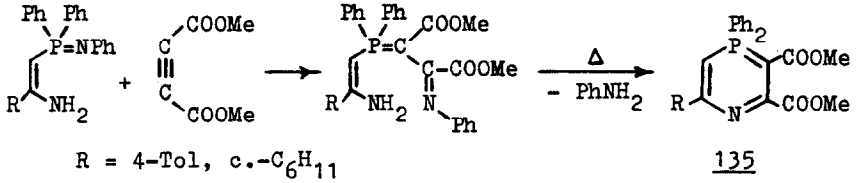
(90)

R = AlkO, Alk_2N

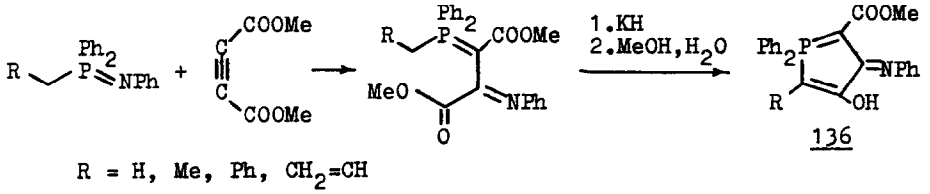
A similar insertion occurs as an initial step in the one-pot synthesis of 2-vinyl-1-azadienes **133** and divinylketones **134** as in Scheme 20[293] as well as azaphosphinines **135** (eqn 91)[294] or phospholes **136** (eqn 92).[295] In the last two cases the intermediate phosphorus ylides undergo intramolecular condensation.



Scheme 20.



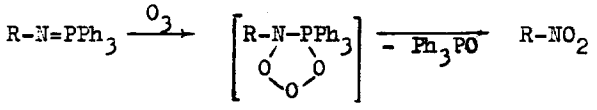
(91)



(92)

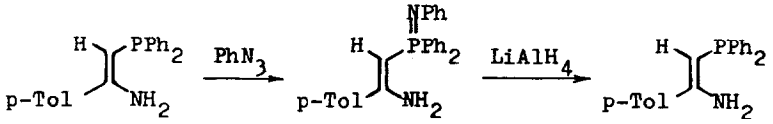
6.5. *Oxidation and reduction*

The oxidation of iminophosphoranes with ozone produces nitro compounds, presumably through an intermediate cycloadduct.[296]



(93)

By reduction of phosphine imines with lithium aluminium hydride, it is possible to obtain starting phosphines, that is, an imino group can be used to protect a P^{III} center[284,285] (eqn 94).[284]



(94)

6.6. *Substitution reactions*

6.6.1. *Substitution of a trimethylsilyl group at imine nitrogen.* A trimethylsilyl group at imine nitrogen usually exhibits a high mobility and is easily substituted. This feature is widely used for chemical modification of iminophosphoranes without affecting their P=N bonds.[1]

Among novel examples of such transformations, the methods for introduction of phosphorus groups to imine nitrogen should be mentioned (eqns 95[297] and 96[19]).

$$R_3P{=}NSiMe_3 + F_3CCH_2O{-}PPh_2 \longrightarrow R_3P{=}N{-}PPh_2 \qquad (95)$$

R = Me, Ph, Me_2N

$$2\ PhPF_4 + 2\ (Me_2N)_3P{=}NSiMe_3 \longrightarrow \left[Ph\text{-}P(F)(N{=}P(NMe_2)_3)_3\right]^{+}\ PhPF_5^{-} \qquad (96)$$

Equation 97 demonstrates the NCO group insertion into Si–N bond of iminophosphorane upon reaction with isocyanate.[298]

$$F_3C\text{-}C(Ph)(N{=}C{=}O)_2 + Me_3Si{-}N{=}PPh_3 \longrightarrow \left[F_3C\text{-}C(Ph)(N{=}C{=}O)\text{-}N(SiMe_3)\text{-}C(=O)\text{-}N{=}PPh_3\right] \xrightarrow{-\ Me_3SiNCO}$$

$$\longrightarrow F_3C\text{-}C(Ph)(N{=}C)\text{-}N(C{=}O)\text{-}N{=}PPh_3 \qquad (97)$$

In recent years, the synthesis of metallocycles on the bases of N-trimethylsilyliminophosphoranes has been actively developed. In eqn 98 and Chart 9 some metallocycles prepared by this method, containing osmium,[299] tungsten,[300] vanadium,[301,302] niobium,[303] titanium,[302] and tellurium[304] are exemplified.

$$Ph_2P(N(SiMe_3))\text{-}PPh_2(N(SiMe_3)) \xrightarrow{OsO_4} Ph_2P(N)\text{-}PPh_2(N)\text{-}Os(=O)_2(OSiMe_3)(OSiMe_3) \qquad (98)$$

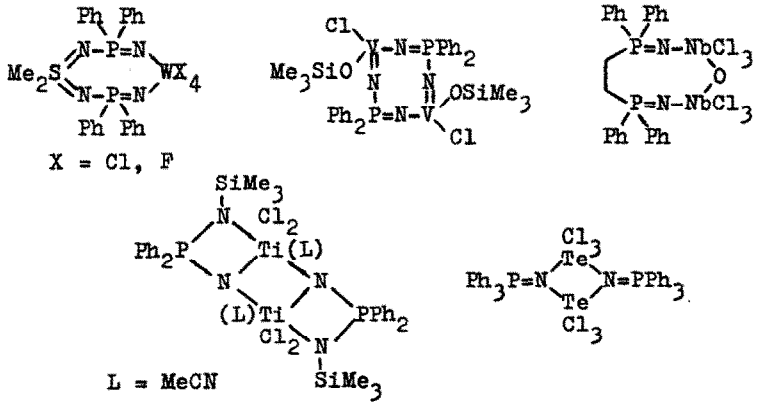
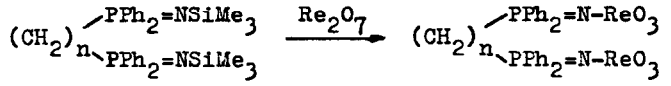


Chart 9.

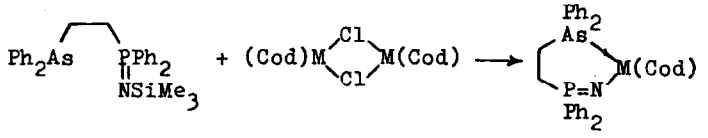
Rhenium substitutes Me_3Si group without cyclization (eqn 99).[305] A similar acyclic mode of substitution is also known for titanium.[306]



(99)

n = 1, 2

N-Trimethylsilyliminophosphoranes are also utilized as ligands in molybdenum, tungsten, rhodium, and iridium coordination compounds[18,307] (eqn 100[307]).



(100)

M = Rh, Ir; Cod = cycloocta-1,5-diene

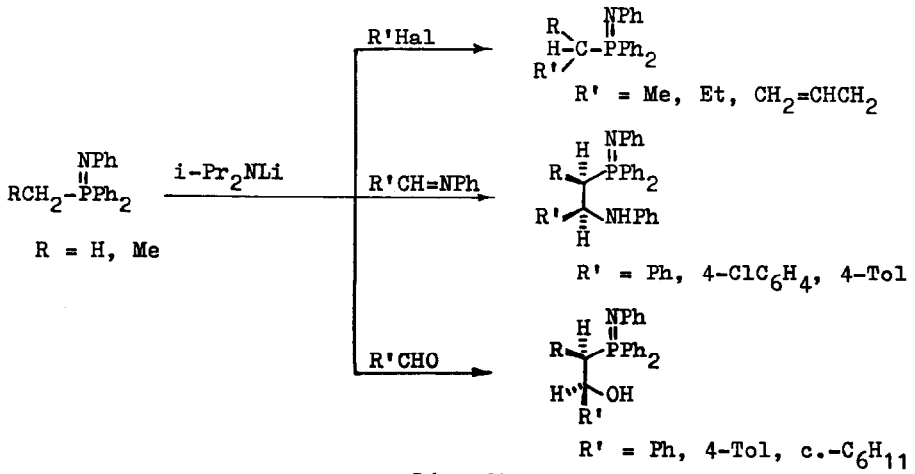
6.6.2. *Functionalization of metallated phosphine imines.* The metallation of alkyldiphenylphosphine imines with lithium diisopropyl amide followed by condensation of an intermediate carbanion with electrophiles is a convenient method for iminophosphorane functionalization at a side chain without affecting the P=N bond. Alkyl halides[308] Schiff bases,[285] aldehydes[309] (Scheme 21) as well as dimethylformamide,[309] dimethyl disulfide,[309] and aryl cyanides[308,310] were used as electrophiles. The reaction with Schiff bases or aldehydes proceeds in a stereoselective manner.

The reaction with aryl nitriles is also stereoselective and is accompanied by a rearrangement resulting in insertion of the nitrile group into the P–C bond (Scheme 22).[310]

Vinyldiphenylphosphine imines can also be alkylated via metallation step.[256] A similar approach was utilized for intramolecular cyclization of phosphine imines[289,295] (eqns 88 and 92).

7. AZA-WITTIG REACTION

The aza-Wittig reaction is one of the most wide-spread methods for conversion of P=N to C=N bond by treating iminophosphoranes with carbonyl or thiocarbonyl compounds.[183] The



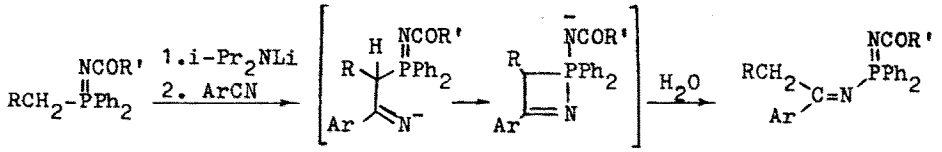
R = H, Me

R' = Me, Et, CH_2=$CHCH_2$

R' = Ph, 4-ClC_6H_4, 4-Tol

R' = Ph, 4-Tol, c.-C_6H_{11}

Scheme 21.



R = H, Me; R' = Ph, EtO; Ar = Ph, 4-Tol, 4-ClC$_6$H$_4$

Scheme 22.

reaction was first described by H. Staudinger;[2,311] however, it is traditionally regarded as an analogue of the well-known Wittig reaction, though the latter, as mentioned by G. Wittig himself, is, indeed, a 'variation on the Staudinger theme'.

In this section, recent examples of acyclic and nitrogen-containing heterocyclic systems prepared by the aza-Wittig reaction are discussed.

7.1. *Intermolecular aza-Wittig reaction*

Scheme 23 presents the types of carbonyl and thiocarbonyl reagents generally employed and the corresponding products formed in the intermolecular version of the aza-Wittig reaction. They include aldehydes[230,238,253,254,312-315] and ketones[316-319] as precursors to Schiff bases; isocyanates[230,253,312,314,320-323] and isothiocyanates[65,312,322] providing carbodiimides; carbon dioxide and carbon disulfide for preparation of isocyanates,[322] isothiocyanates,[230,322,324] phosphine oxides[285,308] or phosphine sulfides;[41,308] and, finally, ketenes[312] converting to ketenimines.

In Chart 10 some representative compounds obtained by this method are shown.

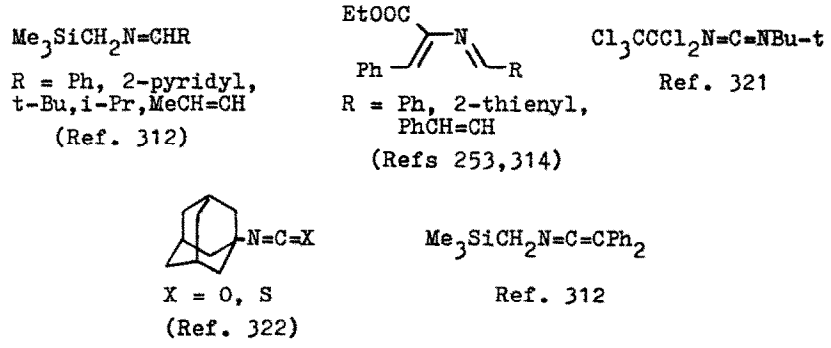
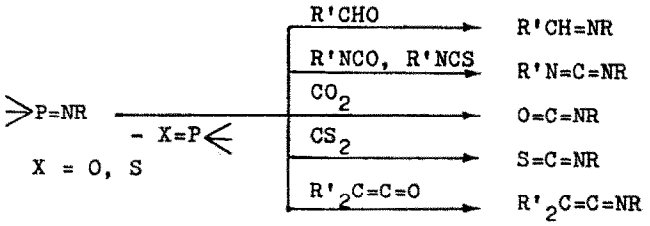
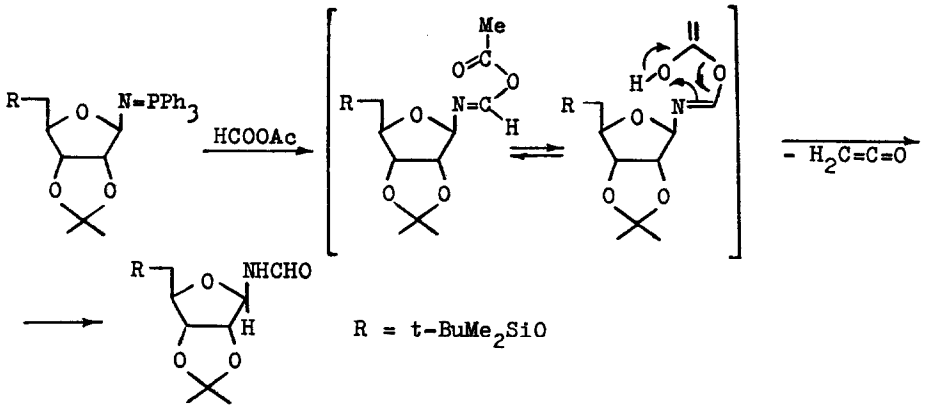


Chart 10.

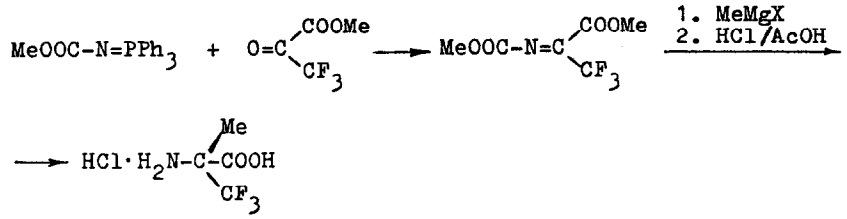


Scheme 23.



Scheme 24.

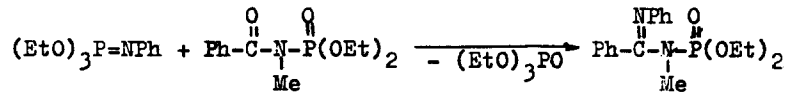
The interesting approach to fluorinated aminoacids via aza-Wittig condensation of phosphine imines and methyl trifluoropyruvate has recently been proposed[316-318] (eqn 101[318]).



(101)

Participation of ester or amide carbonyl groups in the aza-Wittig reaction is not typical. Nevertheless, some examples of its occurrence are known. Using mixed acetic formic anhydride in aza-Wittig condensation it is possible to replace an iminophosphoranyl group with a formamido group.[325]

Amide carbonyl participation in the aza-Wittig reaction is illustrated by eqn 102.[208]



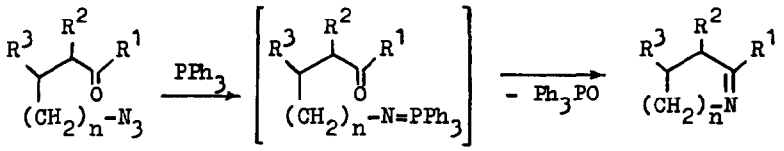
(102)

It is likely that a similar intermolecular mechanism is also operative in the rearrangement shown in eqn 103.[208]

(103)

7.2. *Intramolecular aza-Wittig reaction*

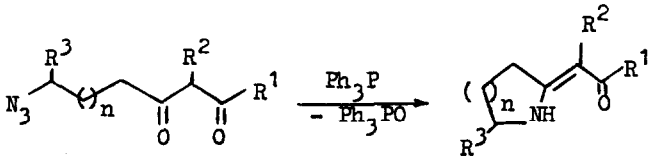
7.2.1. *One-step version.* The intramolecular aza-Wittig reaction takes place on interaction of carbonyl containing azides with phosphorus(III) reagents. It occurs, for example, in ω-azidoketone–triphenylphosphine systems to yield cyclic imines.[326]



(104)

n = 1-3; R^1 = Me, 4-BrC_6H_4; R^2 = H, Me, Et; R^3 = H, PhS

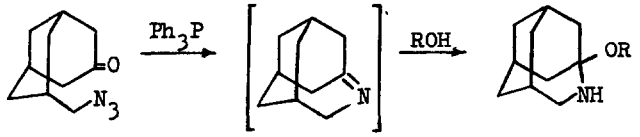
In the case of ω-azido-β-dicarbonyl compounds, the cyclization is followed by hydrogen 1,3-migration to the imine nitrogen[286,327] (eqn 105[327]).



(105)

n = 1-3; R^1 = Me, MeO, EtO; R^2, R^3 = H, Me

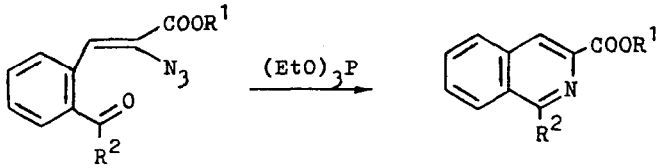
The combination of the Staudinger and aza-Wittig reactions was utilized in the synthesis of 4-azahomoadamantanes.[328,329]



(106)

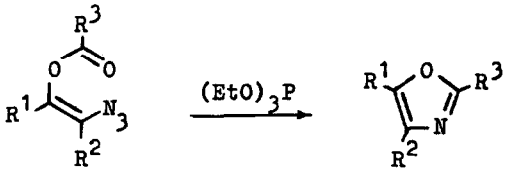
R = Me, Et

With appropriate choice of starting azides, this method provides isoquinolines (eqn 107),[330,331] oxazoles (eqn 108),[332] benzoxazines (eqn 109),[333,334] and many other nitrogen-containing heterocycles.



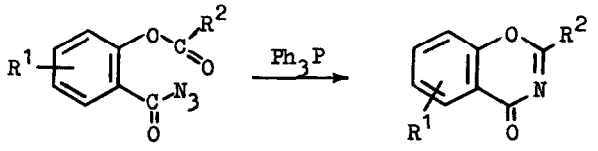
(107)

R^1 = Me, Et, R^2 = H, Me, Ph, HO, EtO



(108)

R^1 = Ar; R^2 = H, Me, i-Pr; R^3 = Me, Et



(109)

R^1 = H, Me; R^2 Me, Ph, AlkO

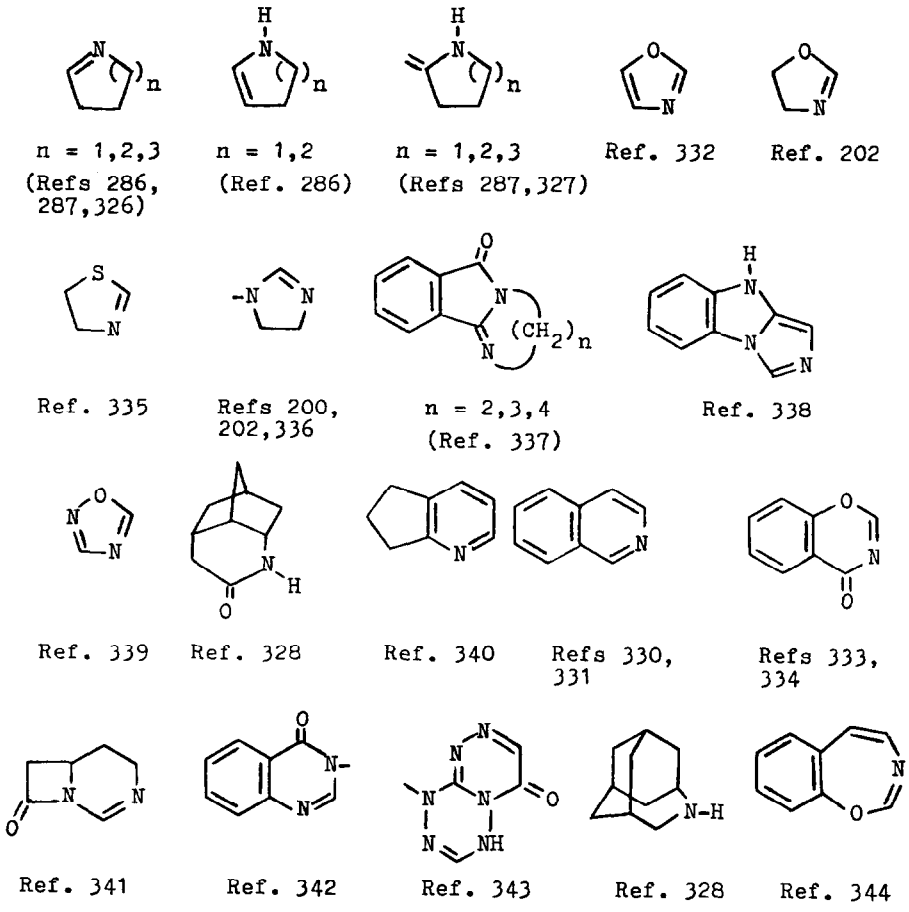
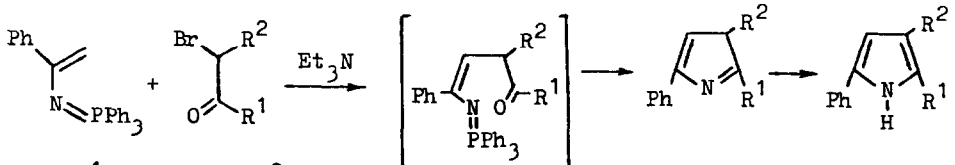


Chart 11.

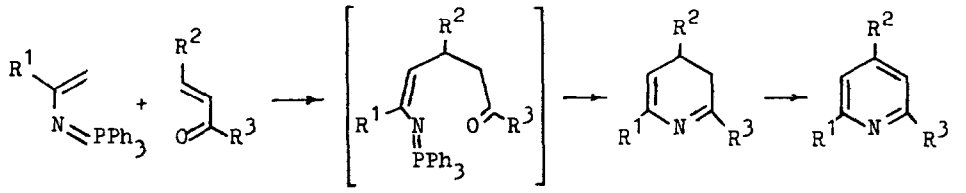
Cyclic structures prepared by this method (Chart 11) illustrate wide synthetic possibilities.

It should be mentioned that a carbonyl function in esters[202,330–335,340] or amides[200,202,336–338,342,343] is more easily subjected to the intramolecular rather than intermolecular aza-Wittig reaction.

7.2.2. *Version with preceding carbonylation of iminophosphoranes.* In this section the heterocycle syntheses are considered starting from *N*-vinyliminophosphoranes, to which a carbonyl function required for intramolecular aza-Wittig condensation was preliminarly introduced. The carbonylation is performed with α-bromoketones in the presence of triethylamine (eqn 110)[345,346] or with α,β-unsaturated ketones via Michael addition (eqn 111).[346–348] The final aza-Wittig condensation provides substituted pyrroles or pyridines, respectively.



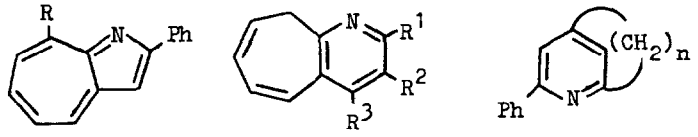
(110)



(111)

R^1 = H, Ph; R^2 = H, Me, Ar; R^3 = Me, Ar

The same approach was also used in synthesis of azaazulenes **137**,[349-351] cyclohepta[*b*]pyridines **138**,[352] and pyridinophanes **139**.[353]



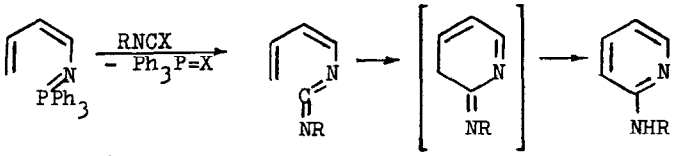
137 **138** **139**

R = H, Me, Bu R^1,R^2,R^3 = H,Me,Ph n = 6-9

Chart 12.

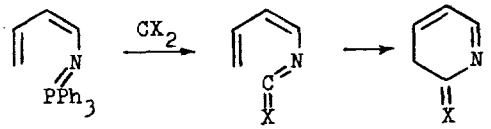
7.3. *Cyclization of aza-Wittig products*

7.3.1. *Electrocyclic ring closure.* This method involves the introduction of a conjugated heterocumulene moiety into iminophosphorane by the aza-Wittig reaction, followed by electrocyclic ring closure (eqns 112–114). In eqns 112 and 113, 1,3-proton shift stabilizes the end cyclic product.



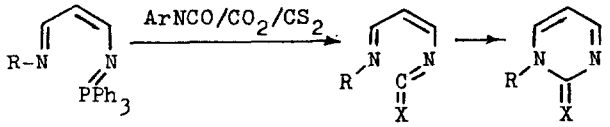
(112)

X = O, S



(113)

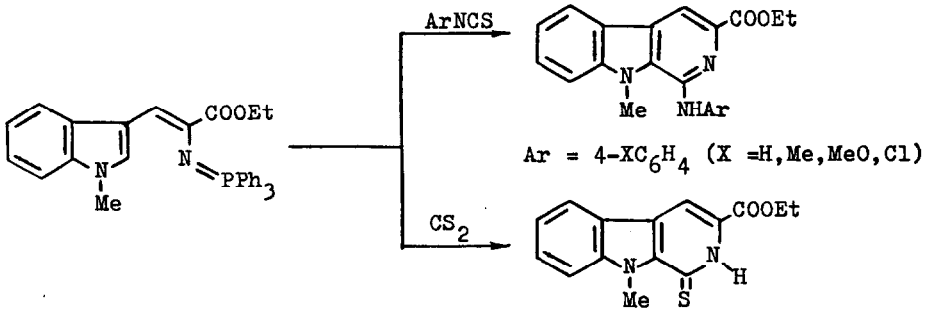
X = O, S



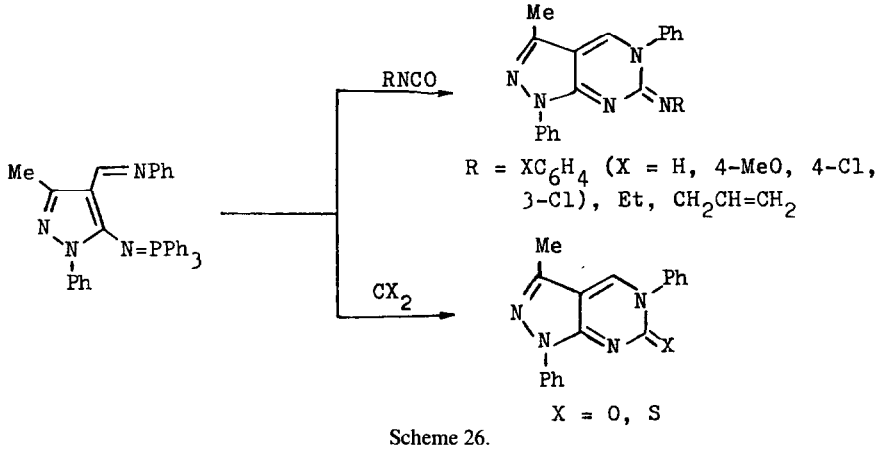
(114)

X = NAr, O, S

In syntheses by eqns 112 and 113, isocyanates,[354-358] isothiocyanates,[359] carbon dioxide[357] or sulfur dioxide[359] are usually employed in an aza-Wittig condensation step. The typical examples are shown in Scheme 25.[359] Other heterocyclic structures, i.e. **140–143**, designed by this method are depicted in Chart 13.



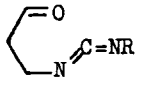
Scheme 25.



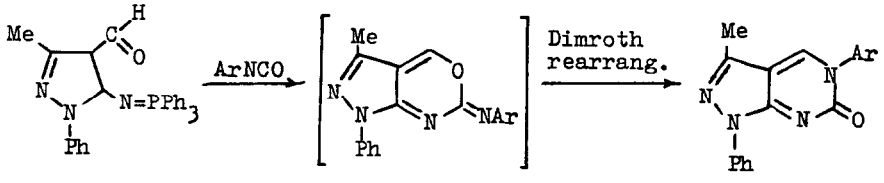
Scheme 26.

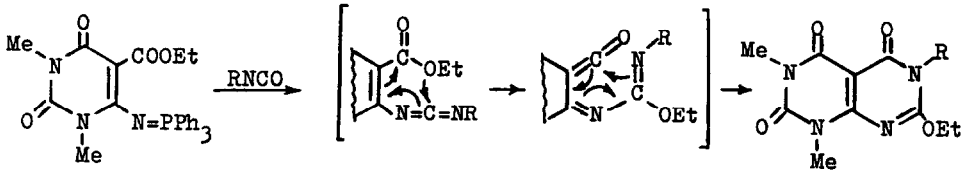
The syntheses according to eqn 114 are exemplified by the following transformations (Scheme 26)[360,361] and by structures **144** and **145** in Chart 13.

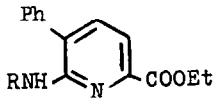
The electrocyclic ring closure in a system pictured below



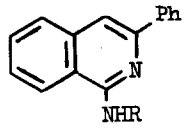
is followed by Dimroth rearrangement,[359,360] as in eqn 115,[360] or includes a preliminary rearrangement of the cumulene moiety (eqn 116).[362]



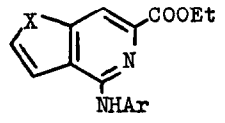




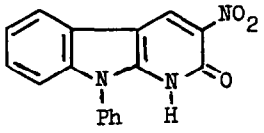
140
Ref. 356



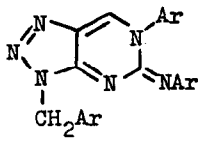
141
Ref. 354



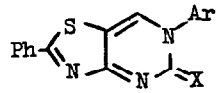
142
X = O,S (Ref. 355)



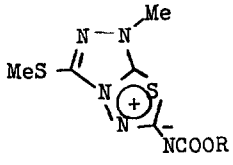
143
Ref. 357



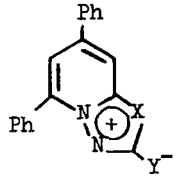
144
Refs 360,361



145
X = O,S,NAr
(Ref. 360)



146
Ref. 364

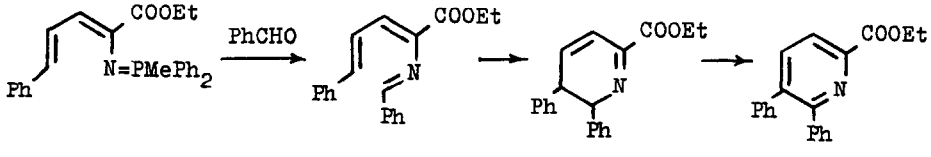


147
X,Y = O,S
(Ref. 363)

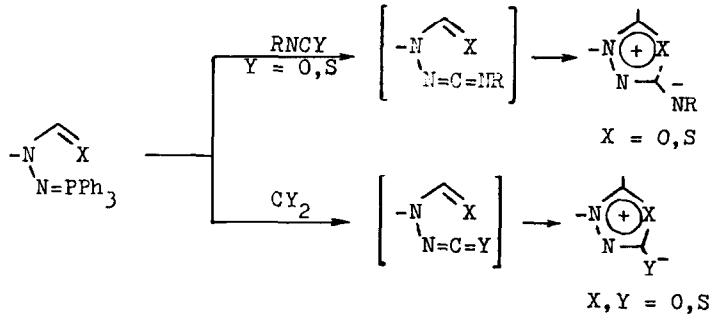
Chart 13.

The method considered here was applied to prepare mesoionic structures, e.g. **146** and **147** in Chart 13, by Scheme 27.[363,364]

The electrocyclization of aza-Wittig products containing no heterocumulene systems can also take place[253,365] (eqn 117[253]).

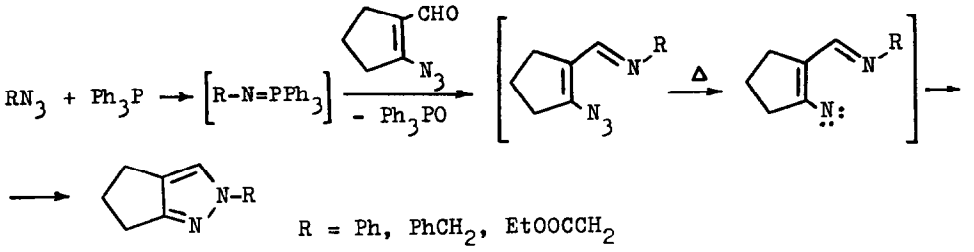


(117)



Scheme 27.

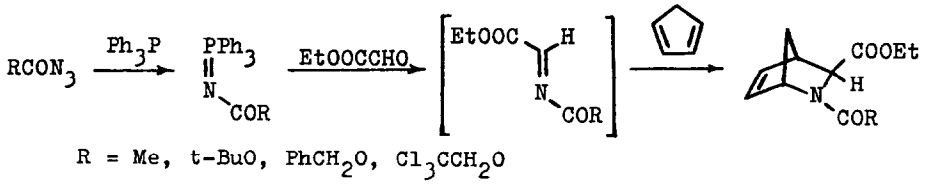
The interesting cyclization of an aza-Wittig imine with participation of a nitrene site has recently been reported.[366]



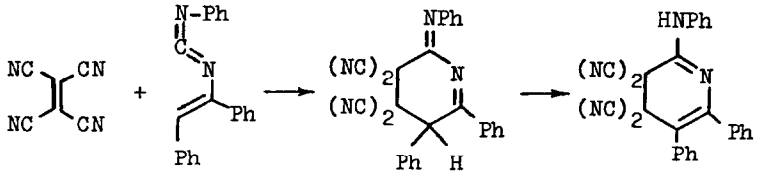
(118)

7.3.2. *Diels–Alder cyclization.* Aza-Wittig condensation products can be used as components of the Diels–Alder cyclization which is, in fact, a variant of the electrocyclic reactions discussed in the preceding section.

Aza-Wittig products can act as dienophiles (eqn 119)[367] or diene components (eqn 120)[354] of intermolecular [4+2]cycloadditions.

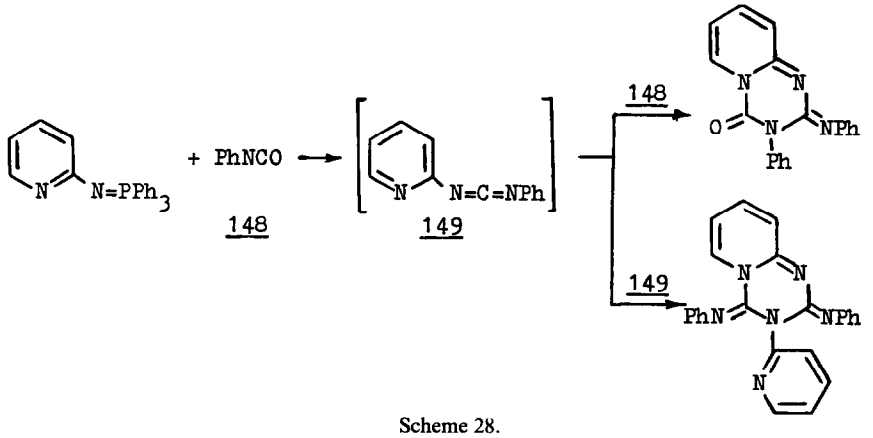


(119)



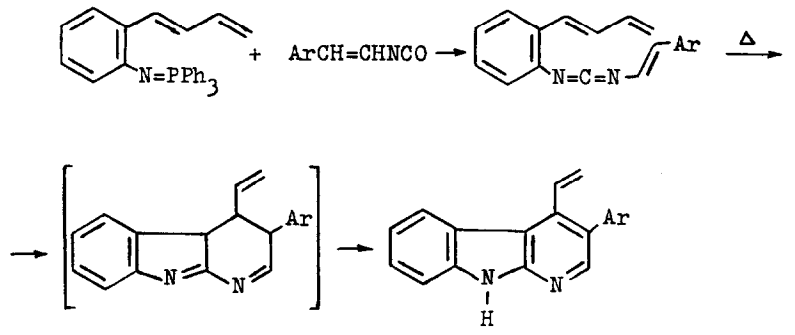
(120)

The competitive [4+2]cycloaddition of the carbodiimide **149** to the identical molecule or to the carbonyl component **148** of the preceding aza-Wittig condensation step, results in formation of two heterocyclic products in the reaction outlined by Scheme 28.[368] Their relative yields depend on molar ratio of the reagents in the aza-Wittig step.



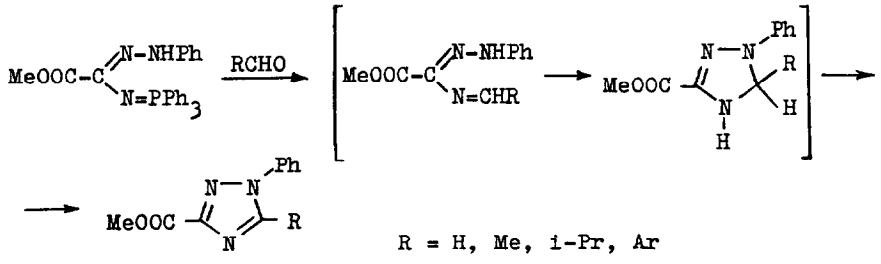
Scheme 28.

In equation 121 the rare example of an intramolecular hetero Diels–Alder cycloaddition is presented. Here, the carbodiimide moiety functions as a part of a 2-azadiene, whereas the C=C double bond of the *ortho*-butadienyl substituent takes a role of a dienophile.[320]

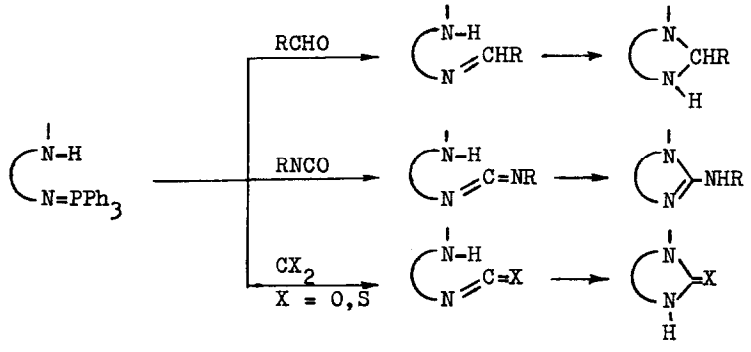


(121)

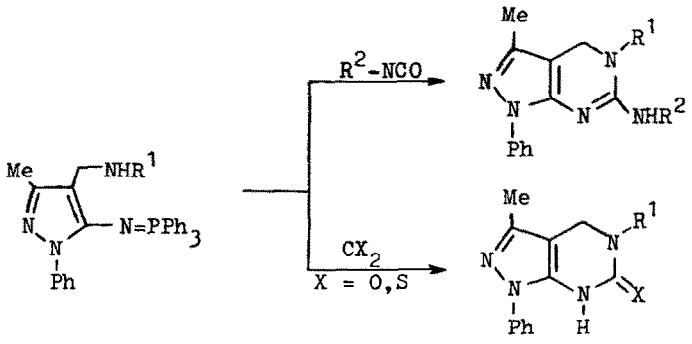
7.3.3. *Cyclization following intramolecular nucleophilic attack.* In this final section some specific examples of heterocycle synthesis based on iminophosphoranes will be considered. It includes a condensation step of the aza-Wittig type and subsequent cyclization involving nucleophilic attack at the imine carbon atom (Scheme 29). The intramolecular nucleophile can be the nitrogen atom of a hydrazono[369–372] (eqn 122),[369] amino (Scheme 30),[373] enamino[101,102,372,374] or amido group (Scheme 31[375]).



(122)

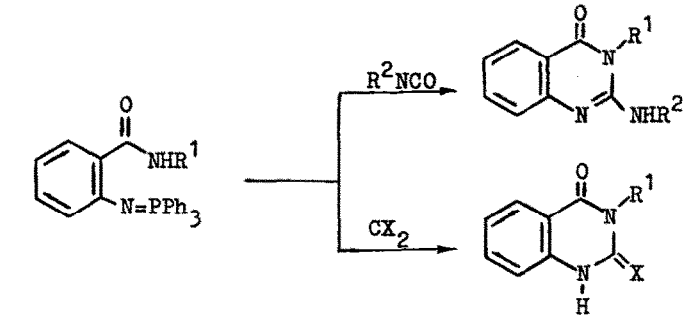


Scheme 29.



R^1 = CH_2=$CHCH_2$, HC≡CCH_2, Ph, 4-Tol
R^2 = 4-Tol, Ph, Et

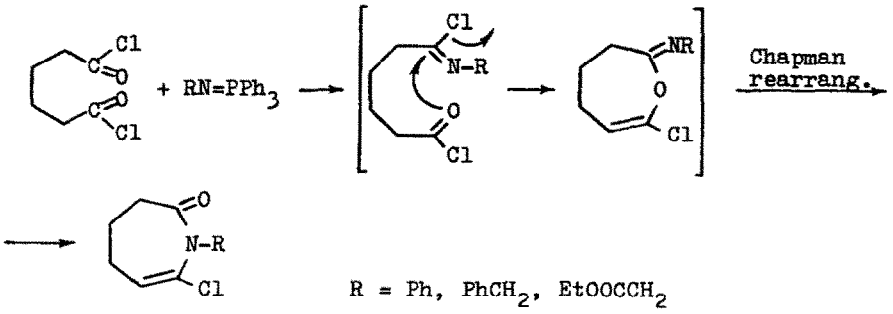
Scheme 30.



R^1, R^2 = Me, Ar; X = O, S

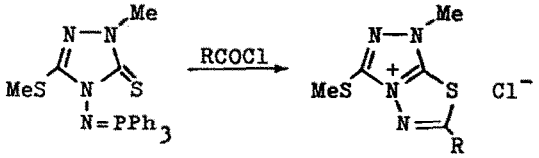
Scheme 31.

In addition, there are some examples of the intramolecular nucleophilic attack at imine carbon involving either carbonyl oxygen (eqn 123),[376] thione sulfur (eqn 124),[364] or a carbon atom (eqn 125).[377]



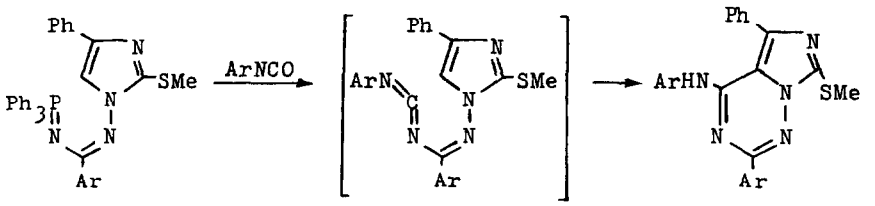
(123)

R = Ph, $PhCH_2$, $EtOOCCH_2$



(124)

R = Me, Ph, PhCH=CH, 1-$C_{10}H_7$



(125)

8. CONCLUSION

We can state with satisfaction that the Staudinger reaction now enters its eighth decade with still unspent potential. It continues to intrigue researchers and stimulates new enterprises in organoelement chemistry.

Two main streams can be distinguished in current publications. The first represents investigations on the Staudinger reaction its mechanism and reagent structure–reactivity relations. For the last decade, a new wave has arisen and strengthened in this stream. This development involves phosphorus in states other than $\lambda^3\sigma^3$ as well as the imination of other hetero-elements with azides. This expansion of the traditional frames of the classical Staudinger reaction has already resulted in the synthesis of numerous new compounds with nitrogen–element bonds.

The second, more abundant stream comprises the utilization of the Staudinger products for preparation of various organic structures containing no phosphorus, including nitrogen heterocycles, cumulenes, amines, amides, and imines. Here, the ideas of the two outstanding scientists, H. Staudinger and G. Wittig, come into contact and give impressive practical results.

Up to now, more than 800 publications on the Staudinger reaction have already appeared in the literature. It is high time to generalize all the information and analyse it in a form which is more comprehensive than is possible in sporadic reviews.

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