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Chemistry of Dihydrophenophosphazines

A.I.Bokanov and B.I.Stepanov

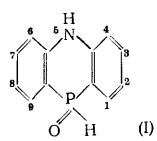
Work during recent years on the synthesis and investigation of 5,10-dihydrophenophosphazines is summarised. It is suggested that these compounds containing tervalent phosphorus may be of interest as pharmacological preparations. A complete list of 5,10-dihydrophenophosphazines synthesised by 1976 is given, together with 40 references.

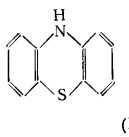
CONTENTS

I. Introduction 855
II. Methods of synthesis 855
III. Reactions of dihydrophenophosphazines 856
IV. Physicochemical properties 857

I. INTRODUCTION

Almost all our knowledge of 5,10-dihydrophenophosphazines has been obtained during the past 16 years, for only 5 papers had been published on them before 1960.[1] In 1890 Michaelis and Schenk reported[2,3] that diphenylamine reacts with phosphorus trichloride at 250°C; elementary analysis of the substance obtained by hydrolysing the reaction mass suggested three possible structures. In 1938 Sergeev and Kudryashov[4] improved the method of preparation, and proved by chemical methods that it had a dihydrophenophosphazine structure. In 1960 the structure of the product obtained by Michaelis et al.[2-5] was finally established: Häring[6] identified it as 5,10-dihydro-10-oxophenophosphazine (I).

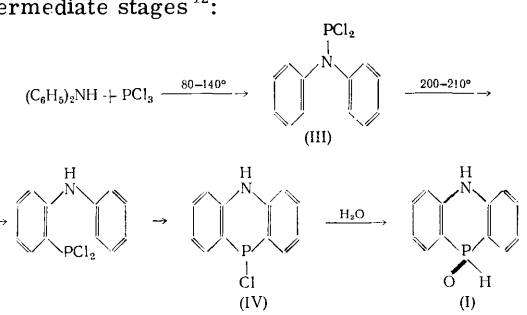

(I)


(II)

5,10-Dihydrophenophosphazines are phosphorus analogues of phenothiazines. Derivatives of phenothiazine (II) are used as antioxidants and therapeutic preparations[7,8]. A few patents have claimed that dihydrophenophosphazines may also find application in analogous fields of technology and medicine[9-11].

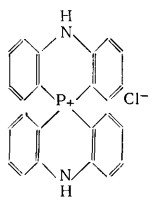
II. METHODS OF SYNTHESIS

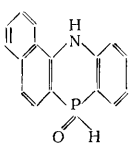
The preparation of dihydrophenophosphazines by the action of phosphorus trichloride on diphenylamine or its homologues has been described in the greatest detail[6,12]. The process is conducted at normal pressure in the absence of a catalyst, by gradually raising the temperature to 200–210°C. The reaction passes through a series of intermediate stages[12]:


(1)

In agreement with the suggested mechanism, the dihydrophenophosphazine (I) has been synthesised[12] by the thermolysis of the previously prepared chloro-amide (III). Intermediate formation of (III) is supported also by the fact that *N*-methyldiphenylamine[13] and *N*-methylditolylamine[12] do not react with phosphorus trichloride under the above conditions. The suggestion that reaction terminates at the formation of 10-chloro-5,10-dihydrophenophosphazine (IV) is less strongly based, since the reaction mass is treated with water in the procedure adopted[4,6,12], and the acid chloride (IV) has not once been isolated. It is possible that the main component of the reaction mixture before hydrolysis is a polymer containing phosphorus–nitrogen bonds, not the acid chloride (IV).

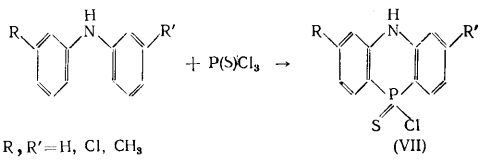
Reaction between diphenylamine and phosphorus trichloride yields a mixture of substances. The chief side-product is 5,5′-dihydro-10,10′-spirobiphenophosphazinium chloride (V).[12,14]


(V)


(VI)

The limits of applicability of reaction (1) have not yet been determined, but naphthylphenylamine is known to react with phosphorus trichloride similarly to diphenylamine, the products being 7,12-dihydro-7-oxobenzo[*c*]-phenophosphazine (VI) and the corresponding spiro-compound[12].

The use of thiophosphoryl chloride has also been suggested for converting diarylamines into 5,10-dihydrophenophosphazines[9]:


(2)

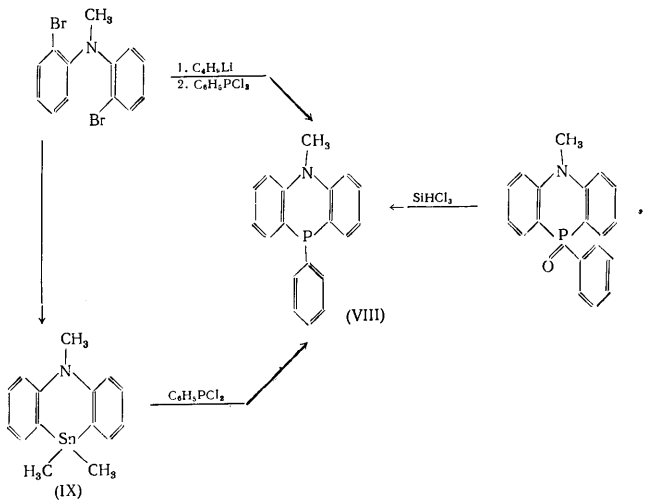
R, R′ = H, Cl, CH_3 (VII)

In contrast to the reaction with phosphorus trichloride, the acid chlorides, 10-chloro-5,10-dihydro-10-thionophenophosphazines (VII), have been isolated and identified. The patent description[9] does not indicate the yields of these compounds (VII), but from other information[1] it appears that, of the two procedures—in the absence of a

solvent under pressure at 200°C or in boiling *o*-dichlorobenzene at normal pressure—the former gives the higher yields.

Derivatives of phenothiazine (II) have found widespread therapeutic use, e.g. as antihistamines [8,15]. Synthetic work on 5,10-dihydrophenophosphazines [6,9,16-18] has been stimulated by the efforts to find new medicinals like phenothiazines. Hitherto these attempts have not achieved real success, which can be explained formally by the fact that only phenothiazines containing bivalent sulphur possess biological activity, whereas the 10-oxo- and 10-thiono-5,10-dihydrophenophosphazines tested [6,9,16-18] are analogues of phenothiazine *S*-oxides. It is more likely that medicinals will be found among phenophosphazines containing a tervalent phosphorus atom.

These latter compounds may be synthesised by analogy with 5,10-dihydro-5-methyl-10-phenylphenophosphazine (VIII): [19-21]

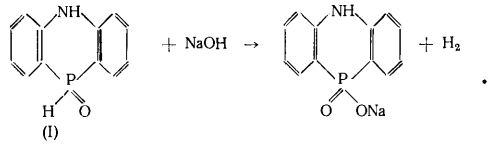


N-Alkyl-*oo'*-dibromodiphenylamines are difficultly accessible, which restricts the possibilities of their use for the synthesis of 5,10-dihydrophenophosphazines [13,19]. The latter can be obtained by replacing the tin atom in heterocycles of the type (IX), [20] which demonstrates the greater thermodynamic stability of phosphorus–carbon than of tin–carbon bonds, but this method is of no synthetic value, since the initial 5,10-dihydrophenazastannines are obtained from the same *oo'*-dibromodiphenylamines. In many cases the most rational method for obtaining dihydrophenophosphazines containing tervalent phosphorus atoms may be reduction [21] of the corresponding *P*-oxides or *P*-sulphides.

III. REACTIONS OF DIHYDROPHENOPHOSPHAZINES

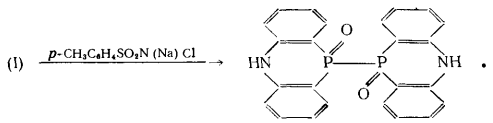
1. Reactions of the Heteroatoms

Derivatives of 5,10-dihydrophenophosphazine are usually obtained from the 10-oxo-compound (I) as starting material. The latter undergoes the reactions characteristic of oxides of secondary phosphines [22]: it adds at an activated multiple bond, and can be alkylated and oxidised at the phosphorus atom. Several methods have been prepared for oxidising (I) to phenophosphazinic acid—with air in boiling tetralin [4,6], or with hydrogen peroxide in acetic acid [6] or in aqueous alkali [12]—but in the last case the use of hydrogen peroxide is not necessary, since boiling aqueous alkali converts the phenophosphazine (I) smoothly into a salt of phenophosphazinic acid [23]:

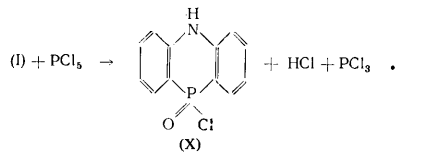


(The mechanism of the oxidation of oxides of secondary phosphines in alkaline media has been discussed in Ref. 24.)

Elementary iodine and chloramine T effect a different course of oxidation, converting (I) into 5,5'-dihydro-10,10'-dioxo-10,10'-diphenophosphazinyl [6]:

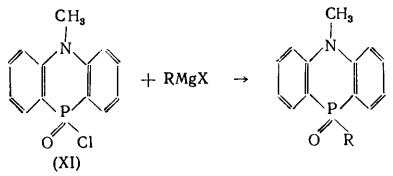


If the final aim is to prepare derivatives of phenophosphazinic acid, it is most rational to use phosphorus pentachloride as oxidant [25]:



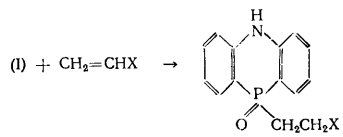
Phenophosphazinic esters and amides can be obtained by replacing the chlorine atom in the acid chloride (X). [6,11,17,25,26] The thio-acid chlorides (VII) undergo analogous reactions with alcohols and amines [1,6,11,17,18], but in this case the products of esterification must be further investigated to differentiate between thionic and thiolic isomers $\diagdown$PS.OR and $\diagdown$PO.SR. [6,18]

The acid chloride (XI) reacts with organomagnesium compounds with the formation of phosphorus–carbon bonds [21]:



R=CH3, C6H5; X=I, Br .

However, most of the phenophosphazines containing exocyclic phosphorus–carbon bonds have been obtained directly from the phenophosphazine (I) by addition to alkenes and azomethines [16,27]. The reaction conditions depend on the structure of the alkene. With acrylic acid and its derivatives, for example, the process is conducted without a solvent and without a catalyst at 140–170°C: [27]



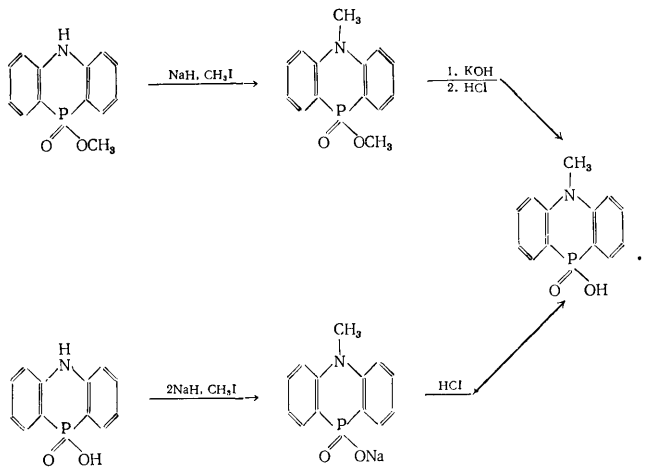
X=COOH, $COOCH_3$, CN .

1-Phenylprop-2-en-1-one adds to (I) in the presence of sodium ethoxide in alcoholic solution at 20°C. [16] At the

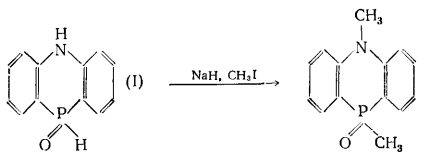
present time no kinetic data are available for a correlation to be sought between the reactivity and the structure of the reactants; moreover, not all the facts can be explained even qualitatively. Thus it has been established[16] that the phenophosphazine (I) does not add to azodicarboxylic ester, but it reacts with the dimorpholide of the acid in boiling ethanol in the absence of catalysts.

Examination of published results[16,27] leads to the preliminary conclusion that the reactivity of multiple bonds towards (I) increases in the sequence N:N < C:C < C:N. Addition takes place at the phosphorus atom independently of the nature of the multiple bond[16,27]. In view of these facts, Häring's conclusion[6] that phenyl isocyanate adds at the nitrogen atom in the phenophosphazine (I) cannot be accepted without proof.

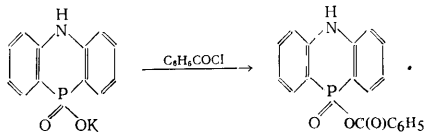
The nitrogen atom can be alkylated[21,23] when its nucleophilic character has been enhanced by ionisation of the imino-group $\rangle NH \rightarrow \rangle N^-$:



Under the corresponding conditions the phenophosphazine (I) yields a dimethylated product[21]:



When protolysis of the nitrogen–hydrogen bond is excluded, the nucleophilicity of the imino-group is extremely low. Thus a phenophosphazinate salt undergoes benzoylation at the oxygen atom, not at the nitrogen atom[6]:

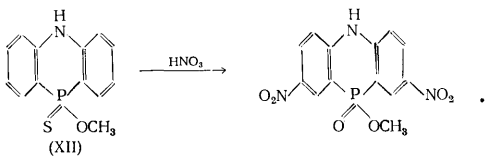


Thus the activity of the nucleophilic centres in dihydrophenophosphazines diminishes in the sequence $\rangle N^- > \rangle PO.O^- > \rangle NH$.

2. Electrophilic Aromatic Substitution

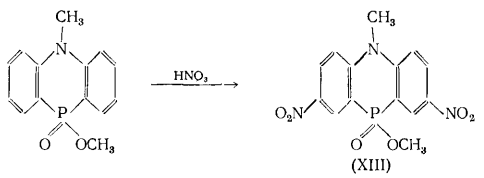
At 5°C molecular bromine in formic acid oxidises 5,10-dihydro-10-oxophenophosphazine (I) and simultaneously brominates its benzene rings[6], forming a mixture of products of different degrees of bromination, among which a dibromo-5,10-dihydro-10-hydroxy-10-oxophenophosphazine (dibromophenophosphazinic acid) predominates in which the positions of the bromine atoms have not been established. It is not known whether phenophosphazinic acid is brominated under the same conditions, and therefore the sequence of oxidation and substitution is obscure.

According to McHattie[1] the 10-thionophenophosphazine (XII) does not react with the *p*-nitrobenzenediazonium ion, whereas in boiling nitric acid it undergoes simultaneous nitration and oxidation:



(XII)

Nitration of 5,10-dihydro-10-methoxy-5-methyl-10-oxophenophosphazine in acetic acid yields the dinitro-product (XIII), whose structure has been proved unambiguously by proton magnetic resonance[23]:



(XIII)

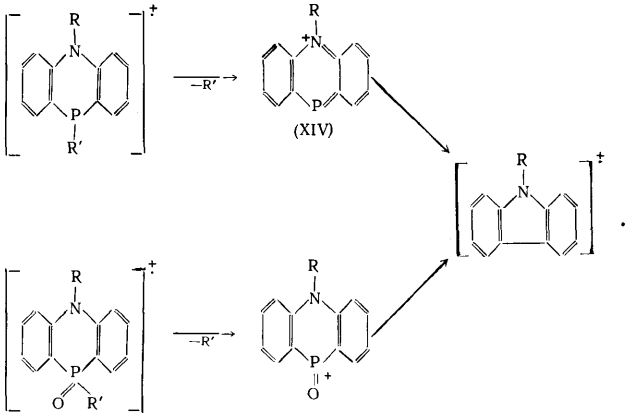
IV. PHYSICOCHEMICAL PROPERTIES

Since 1960 the infrared spectra have been used to identify dihydrophenophosphazines. In no case have the vibrations been calculated, and the frequencies representing vibrations of the heterocycle have not been identified. Investigators working with 5,10-dihydro-10-oxophenophosphazines usually mention the frequency of the P=O bond[6,12,18,21,23]. The frequency of stretching vibrations of this bond is lower in dihydrophenophosphazines containing imino-groups, perhaps owing to formation of intermolecular hydrogen bonds, and appears in the range 1150 to 1195 cm^{-1}.[12,18] Alkylation of the nitrogen raises the frequency to 1180–1240 cm^{-1}.[21,23] Thus the original assignment[6] of bands at 1340–1350 cm^{-1} to vibrations of the P:O bond is incorrect.

Among nuclear magnetic resonance methods only proton resonance has been used to investigate 5,10-dihydrophenophosphazines, mainly to identify alkyl groups attached to the nitrogen and phosphorus atoms[12,20,21]. In the ^1H n.m.r. spectrum of the dinitro-compound (XIII), however, the chemical shifts of non-equivalent aromatic protons differ so considerably that the spectrum in this region could be completely deciphered[23]. The spin–spin interaction constants in the (XIII) molecule, $^3J(PH) = 14.0$ and especially $^4J(PH) = 7.2$ Hz, are considerably larger than those in triphenylphosphine oxide and its substituted derivatives, where the corresponding values are 11.2–12.4 and 1.8–2.7 Hz.[28,29]

Data have been published on the mass spectra of individual dihydrophenophosphazines[12,21,23,30]. The main

routes by which these compounds break down can be represented by the scheme

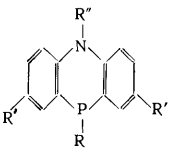


The ion (XIV) is the chief product in the mass spectra of the tervalent phosphorus derivatives, even with ionising radiation of energy 30 eV.[21] Oxidation of the phosphorus atom enhances the stability of the molecular ion, which is usually the main product in the spectra of 5,10-dihydro-10-oxophenophosphazines.

Table 1. Electronic spectra of 10-substituted (R) 5,10-dihydro-5-methyl-10-oxophenophosphazines[21].

R	Solvent	λ_{max}, nm (lg ε)			
CH_3	alcohol	220 (4.50)	273 (4.25)	301 (3.92)	327 (3.76)
C_6H_5	alcohol	226 (4.50)	275 (4.15)	306 (3.81)	336 (3.80)
OCH_3	alcohol	223 (4.21)	272 (4.31)	299 (4.00)	337 (3.80)
Cl	dioxan	231 (4.44)	273 (4.23)	305 (3.95)	346 (3.81)

Table 2. 5,10-Dihydrophenophosphazines



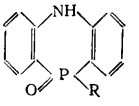
R	R′	R″	M.p., °C	Identification	Ref.
OC_2H_5	H	H	151.5—152	—	4
CH_3	H	CH_3	102—103	methiodide, infrared, ^{1}H nmr, ultraviolet spectra	21
C_6H_5	H	CH_3	159—160	methiodide, infrared, ^{1}H nmr, ultraviolet spectra	10, 19—2
C_6H_5	Br	CH_3	227—229	infrared, ^{1}H nmr, ultraviolet spectra	20, 21
C_6H_5	H	C_2H_5	96.5—98	—	10, 19
C_6H_5	CH_3	CH_3	144—146	infrared, ^{1}H nmr, ultraviolet spectra	20

In the opinion of Freedman and Styles[31] the ultraviolet spectra of phenophosphazinic acids indicate conjugation of a quinquevalent phosphorus atom with the π-electron system of aromatic rings. Table 1 shows that the character of the spectrum, and hence of conjugation in phenophosphazines, is little affected by the nature of substituents attached to the phosphorus atom.

The adiabatic ionisation potentials of four dihydrophenophosphazines have been determined[32] by photoionisation mass spectroscopy. The values of 6.90 ± 0.05 eV obtained for 5,10-dihydro-5-methyl-10-phenylphenophosphazine (VIII) lies within the range given for *N*-methylphenothiazine (6.60—6.96 eV [33,34]). Since the pharmacological activity of phenothiazines is attributed to their low ionisation potentials[34,35], it is very likely that pharmacological products can be based also on 5,10-dihydrophenophosphazines.

Tables 2—5 contain a complete list of all the 5,10-dihydrophenophosphazines reported in periodicals, patents,

Table 3. 5,10-Dihydro-10-oxophenophosphazines

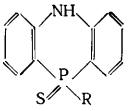


R	M.p., °C	Identification	Ref.
H	215—216	Ti, U salts	4,5
H	219—222	ultraviolet spectrum	11
H	214—216	hydro-bromide, -chloride, ultraviolet, infrared spectra	6,12
OH	above 250	Ag salt	4
OH	270—274	ultraviolet spectrum	12,31
OH	274—275	K salt, infrared spectrum	6,23
OH	284—286	〃	1
Cl	290 (decomp.)	infrared spectrum	6,25
OCH_3	112—114	—	4
OCH_3	224—225	infrared spectrum	6,23
SCH_3	265—267	infrared spectrum	6,18
SCH_3	275—276	ultraviolet spectrum	11
C_4H_5	—	mass spectrum	30
$NHCH_2CH_2OH$	232	—	17
OC_2H_5	99	—	4
OCH_2CH_2Cl	—	—	36
SC_2H_5	221—222	infrared spectrum	18
CH_2CH_2COOH	245—246	—	27
CH_2CH_2CN	226—227	—	27
$NHCH_2CH{=}CH_2$	254	—	17
NHC_3H_7	254	—	17
SC_3H_7-n	174—176	infrared spectrum	18
$CH_2CH_2C(O)CH_3$	195—196	—	27
$CH_2CH_2COOCH_3$	162—163	—	27
$CH(CH_3)CH_2COOH$	148—149	—	27
$-CHC(O)OC(O)CH_2-$	247	—	27
NHC_4H_9	238	—	17
$N(C_2H_5)_2$	244	—	17
$-N(CH_2CH_2)_2O$	250	ultraviolet spectrum	11
OC_4H_9	139.5—141	ultraviolet spectrum	6,11
SC_4H_9	149—151	infrared spectrum	17
$NH(CH_2)_3N(CH_3)_2$	185—186	—	6
$-N(CH_2CH_2)_2NCH_3$	230—235	—	26
$-CHCOOCH_3$ CH_2COOCH_3	208—209	—	27
NHC_6H_5	241	—	17
$NHCH_2CH_2N(C_2H_5)_2$	191—194	methiodide	6
$OCH_2CH_2N(C_2H_5)_2$	80—83.5	methiodide	6
$OCH_2C_6H_5$	179—180	—	6
$OC(O)C_6H_5$	above 340	infrared spectrum	6
$O(CH_2)_3N(C_4H_9)_2$	42—43.5	—	6
$CH(C_6H_5)CH_2C(O)CH_3$	181—183	—	27
$CH(C_6H_5)CH_2COOCH_3$	133—135	—	27
$CH(C_6H_5)CH(CN)CONH_2$	281—283	—	16
$-N-C(O)N(CH_2CH_2)_2O$ $NHC(O)N(CH_2CH_2)_2O$	200 (sinters)	—	16
$O{=}P(C_6H_4)_2NH$ *	above 300	infrared spectrum	6
$-O(O)P(C_6H_4)_2NH$ **	above 300	infrared spectrum	6
$CH(C_6H_5)NHC_6H_5$	182—185	—	16
$CH(C_6H_5)NHSO_2C_6H_5$	190—191	—	16
$CH(C_6H_5)CH_2C(O)C_6H_5$	242—244	—	16
$CH(COC_6H_5)CH_2C(O)C_6H_5$	232—233	—	16

* 5,5′-Dihydro-10,10′-dioxo-10,10′-biphenophosphazinyl.
** Phenophosphazinic anhydride.

and deposited papers† by the beginning of 1976. They do not include compounds for which the original source gives neither constants nor elementary analyses. Spirobiphenophosphazines are also omitted: all the information on these compounds will be found in papers by Jenkins and Freedman [12,14].

Table 4. 5,10-Dihydro-10-thionophenophosphazines



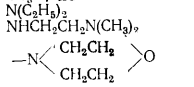
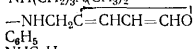
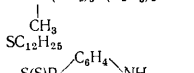
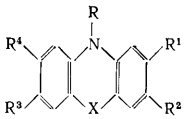
R	M.p., °C	Identification	Ref.
Cl	252—254	—	9
Cl	229 5—237.5	—	6
OH	213	K salt, infrared spectrum	6,18
OH	215	ultraviolet spectrum	11
OH	320—322	triethylamine, piperazine salts	1
NH_2	233—235	—	1
$NHNH_2$	240—241	—	1
SH	322—326	pyridine, piperazine salts	1
OCH_3	184—185.5	infrared spectrum	6
OCH_3	186—187	—	18
OCH_3	194—195	—	1
$N(CH_3)_2$	276—278	—	1
$NHCH_2CH_2OH$	185	—	17
OC_2H_5	207—208	—	1
OC_2H_5	211—212	—	18
OC_2H_5	213—214	ultraviolet spectrum	11
OCH_2CBr_3	193—194	—	1
OCH_2CH_2OH	208—209	—	1
$NHCH_2CH{=}CH_2$	251	—	17
NHC_3H_7	238—239	—	17
OC_3H_7-n	178—180	—	1,18
OC_3H_7-iso	233—234	—	18
OC_3H_7-iso	242—244	—	1
$N(C_2H_5)_2$	184	—	17
$NHCH_2CH_2N(CH_3)_2$	142—144	—	1
	275—276	ultraviolet spectrum	11
NHC_4H_9-n	206—207	—	1
OC_4H_9-n	130—131	—	1
$OCH_2CH_2N(CH_3)_2$	167—169	methiodide	1
$NH(CH_2)_3N(CH_3)_2$	122—124	—	1
	199—200	—	1
C_6H_5	268—269	—	1
NHC_6H_5	247—248	—	1
NHC_6H_5	238—240	—	17
OC_6H_5	222—224	—	1
OC_6H_4Cl-p	204—206	—	1
$OC_6H_4NO_2$-p	250—252	—	1
$SC_6H_4NO_2$-p	259—260	—	1
$NHCH_2C_6H_5$	184	—	1
$OC_6H_4CH_3$-o	164—166	—	1
$NHCH(CH_3)_3N(C_2H_5)_2$ | CH_3	135—136	—	1
$SC_{12}H_{25}$	92—93	ultraviolet spectrum	11
	320—322	—	1

Table 2 lists dihydrophenophosphazines containing a tervalent phosphorus atom; Tables 3 and 4 give dihydrophenophosphazines derived from quinquevalent phosphorus, with both the nitrogen atom and the benzene rings unsubstituted; and Table 5 contains the remaining dihydrophenophosphazines with a quinquevalent phosphorus atom. Within each table the compounds are arranged in order of increasing number of carbon atoms in the molecule. The columns headed "identification" list the simple derivatives (salts, hydrochlorides, methiodides) and spectral methods by which the compounds have been characterised.

† McHattie's results are quoted in the book by Mann [1].

Table 5. Substituted 10-oxo- and 10-thiono-5,10-dihydrophenophosphazines



X	R	R^1	R^2	R^3	R^4	M.p., °C	Identification	Ref.
P(O)OH	H	H	NO_2	H	H	—	—	4
P(O)H	H	H	CH_3	H	H	205—206	infrared spectrum	12
P(O)OH	H	H	CH_3	H	H	270—272	infrared spectrum	12
P(O)OH	CH_3	H	H	H	H	252.5—253	infrared, ultraviolet spectra	21,23
P(O)OH	CH_3	H	NO_2	NO_2	H	above 320	infrared spectrum	23
P(O)Cl	CH_3	H	H	H	H	217—220	infrared, ultraviolet, ^1H nmr spectra	21
P(O)Cl	CH_3	H	NO_2	NO_2	H	264—267	—	23
$P(O)OCH_3$	H	H	NO_2	NO_2	H	344—345	—	1
P(O)H	H	H	CH_3	CH_3	H	above 400	infrared spectrum	12
P(O)OH	H	H	CH_3	CH_3	H	289 (decomp.)	infrared spectrum	12
$P(O)OCH_3$	CH_3	H	H	H	H	164—165	^1H nmr, infrared, ultraviolet spectra	21
$P(O)OCH_3$	CH_3	H	NO_2	H	H	147—149	^1H nmr, infrared, ultraviolet spectra	23
$P(O)OCH_3$	CH_3	H	NO_2	NO_2	H	275—277	^1H nmr, infrared, ultraviolet spectra	23
$P(O)CH_3$	CH_3	H	H	H	H	205—207	^1H nmr, infrared, ultraviolet spectra	21
P(O)OH	CH_3	H	CH_3	CH_3	H	276—277	infrared, ^1H nmr, ultraviolet spectra	12,31
P(O)H *	H	H	H	H	C_4H_4	238—240	infrared spectrum	12
P(O)OH	H	H	H	H	C_4H_4	290—295	infrared spectrum	12
P(O)H	C_6H_5NHCO	H	H	H	H	227 (decomp.)	—	6
$P(O)C_6H_5$	CH_3	H	H	H	H	162—163	infrared, ^1H nmr, ultraviolet spectra	21
$P(O)C_6H_5$	CH_3	H	Br	Br	H	220—222	^1H nmr, infrared, ultraviolet spectra	21
P(S)Cl	H	Cl	H	H	H	270—272	—	9
P(S)Cl	H	CH_3	H	H	CH_3	283—285	—	9
$P(S)OCH_3$	H	H	CH_3	H	H	250—260	—	1
$P(S)OC_2H_5$	H	Cl	H	H	H	190—192	—	1
$P(S)OC_2H_5$	H	H	Cl	H	H	178—180	—	1
$P(S)OCH_3$	CH_3CO	H	H	H	H	132—134	—	1
$P(S)OCH_3$	H	CH_3	H	H	CH_3	228—230	—	1
$P(S)OC_2H_5$	CH_3CO	H	H	H	H	101—103	—	1
$P(S)OC_2H_5$	H	CH_3	H	H	CH_3	228—230	—	1

*7,10-Dihydro-7-oxobenzo[*c*]phenophosphazine (VI).

ADDENDUM

Four more papers on dihydrophenophosphazines appeared [37-40] while the manuscript was being prepared for press. The Reviewers have collaborated with Bychkov [37] in developing a simple and effective method for synthesising phenophosphazinic acid. The proton magnetic resonance spectrum of the dinitro-compound (XIII), described in a deposited paper [23], has now been published in a more accessible source [38]. X-Ray examination of 5,10-dihydro-5-methyl-10-phenylphenophosphazine (VIII) shows that the molecule is not planar, the angle between the planes of the phenylene rings being 145° [39].

Petrov et al. [40] have improved the method of isolating the phenophosphazine (I) from the mixture of products of reaction (1). 5,10-Dihydro-10-oxophenophosphazines containing hydroxymethyl and aminomethyl groups attached to the phosphorus atom have been obtained from this compound (I), and the infrared spectra have been discussed in detail [40].

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