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Some Considerations Regarding the Nomenclature of Organic Phosphorus Compounds

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The old American, British and German nomenclatures of organic phosphorus compounds and the new Anglo-American proposals are discussed, and the new Swedish proposals are presented. The Swedish nomenclature is based on the designation of all organic derivatives of tervalent phosphorus as *phosphines*, and all derivatives of quinquevalent phosphorus containing oxygen as *phosphine oxides*, or alternatively as derivatives of *phosphoryl* compounds.

The chemistry of organic phosphorus compounds, long a borderline between organic and inorganic chemistry, has in recent years attracted considerable interest. The vast number of compounds synthesized by the German chemist Michaelis [1] during the latter half of the nineteenth century, and by Arbusow [2] in Russia in the beginning of this century, have, for purely academic reasons, once more assumed current interest owing to their applicability as solvents, surfaceactive agents, lubricating-oil additives, plasticizers, insecticides, drugs, and, with regard to the most toxic members of the group, as war gases. In the forefront is the advent of a series of new insecticides, synthesized by Schrader [3], some of which show entirely new properties as chemotherapeutic agents for plants.

The use of these compounds by chemists, biochemists, pharmacologists, and technicians in different countries calls for the use of a readily understandable international nomenclature. However, there is considerable confusion in this respect, not only on the international plane but also in individual countries. To facilitate a survey of the profusion of names in current use, Table 1 has been drawn up containing 37 compounds and their designations in the U.S.A., Britain, and Germany. The U.S.A. is represented not only by Chemical Abstracts [4] but by Kosolapoff [5], who in his book "Organophosphorus Compounds" has proposed a nomenclature somewhat differing from that of Chemical Abstracts. Britain is represented by British Chemical Abstracts, and Germany by Beilstein [6]. As regards Beilstein's nomenclature, only the names

Table 1. Examples of the old American, British and German

Formula	Present name in		
	USA I [4]	USA II [5]	Britain
RPH_2	Alkylphosphine	Alkylphosphine	Alkylphosphine
$RP=O$	—	—	—
$RP=NR$	—	—	—
$RP(OH)_2$	Alkanephosphonous acid	Alkanephosphonous acid	Alkylphosphinic acid
$RP(OR)_2$	Dialkyl alkanephosphonite	Dialkyl alkanephosphonite	Dialkyl alkylphosphinate
$RP(OR)Cl$	Alkyl alkanechlorophosphinite	Alkyl alkanechlorophosphinite	—
$RP(OR)(NR_2)$	Alkyl dialkylamidoalkanephosphinite	Alkyl dialkylamidoalkanephosphinite	—
$R_2P(OH)$	Dialkylphosphinous acid	Dialkylphosphinous acid	Dialkylphosphinous acid
$R_2P(OR)$	Alkyl dialkylphosphinite	Alkyl dialkylphosphinite	Alkyl dialkylphosphinite
R_2PCl	Dialkylphosphinous chloride	Dialkylchlorophosphine	—
$R_2P(NR_2)$	Dialkyl-dialkylphosphinous amide	Dialkyl-dialkylphosphine amide	Dialkyl-dialkylaminophosphine
$(RO)_3P$	Trialkylphosphite	Trialkylphosphite	Trialkylphosphite
$(RO)_2PCl$	Dialkyl chlorophosphite	Dialkyl chlorophosphite	Dialkoxychlorophosphine
$(RO)(R_2N)PCl$	Alkyl dialkylamidochlorophosphite	Alkyl-chloro-dialkylamidophosphite	—
$(RO)P=NR$	Alkoxyalkyliminophosphine	Alkyl-alkylimidophosphite	Alkoxyalkyliminophosphine
R_4PCl	Tetralkylphosphonium chloride	Tetralkylphosphonium chloride	Tetralkylphosphonium chloride
R_3PO	Trialkylphosphine oxide	Trialkylphosphine oxide	Trialkylphosphine oxide
$R_3P=NR$	Trialkyl-alkylphosphine imide	Trialkylphosphine alkylimine	Trialkylphosphine alkylimine
$RPO(OH)_2$	Alkanephosphonic acid	Alkanephosphonic acid	Alkylphosphonic acid
$RPO(OR)_2$	Dialkyl alkanephosphonate	Dialkyl alkanephosphonate	Dialkyl alkylphosphonate
$RPO(OR)Cl$	Alkyl alkanechlorophosphonate	Alkyl chloroalkanephosphonate	Alkylalkoxychlorophosphine oxide
$RPOCl_2$	Alkanephosphonic dichloride	Alkanephosphonyl dichloride	Alkyldichlorophosphine oxide
$RPO(OR)(NR_2)$	Alkyl dialkylamidoalkanephosphonate	Alkyl dialkylamidoalkanephosphonate	Alkylalkoxydialkylaminophosphine oxide
$RPO(NR_2)Cl$	Dialkylamidoalkanephosphonic chloride	Chlorodialkylamidoalkanephosphonate	Alkylchlorodialkylaminophosphine oxide
$R(RO)_2P=NR$	Dialkyl alkylimidoalkanephosphonate	Dialkyl alkylimidoalkanephosphonate	—
$RHPO(OH)$	Alkanephosphinic acid	Alkanephosphonic acid	Alkylphosphonous acid
$R_2PO(OH)$	Dialkylphosphinic acid	Dialkylphosphonic acid	Dialkylphosphonous acid
$R_2PO(OR)$	Alkyl dialkylphosphinate	Alkyl dialkylphosphonate	Alkyl dialkylphosphonite
R_2POCl	Dialkylphosphinic chloride	Dialkylphosphonyl chloride	Dialkylchlorophosphine oxide

nomenclatures and the new Anglo American and Swedish proposals.

Present name in	Suggested name in	
Germany [6]	USA and Britain [7]	Sweden
Alkylphosphin	Alkylphosphine	Alkyl-phosphine
Alkylphosphinigsäureanhydrid	Alkyloxophosphine	Alkyl-oxophosphine
—	Alkyl(alkylimino)phosphine	Alkylimino-alkyl-phosphine
Alkylphosphinigsäure	Alkylphosphonous acid	Alkyl-dihydroxy-phosphine
Alkylphosphinigsäure-dialkyl-ester	Dialkyl alkylphosphonite	Dialkoxy-alkyl-phosphine
Alkylphosphinigsäure-alkylester-chlorid	Alkyl alkylphosphonochloridite	Alkoxy-alkyl-chloro-phosphine
Alkylphosphinigsäure-alkylester-dialkylamid	Alkyl dialkyl-alkylphosphon-amidite	Dialkylamino-alkoxy-alkyl-phosphine
Dialkylhydroxyphosphin	Dialkylphosphinous acid	Dialkyl-hydroxy-phosphine
Dialkylalkoxyphosphin	Alkyl dialkylphosphinite	Alkoxy-dialkyl-phosphine
Dialkylphosphin-chlorid	Dialkylphosphinous chloride	Dialkyl-chloro-phosphine
Dialkyl-dialkylamino-phosphin	Dialkyl-dialkylphosphinous amide	Dialkylamino-dialkyl-phosphine
Trialkylphosphit	Trialkyl phosphite	Trialkoxy-phosphine or trialkyl phosphite
Dialkylphosphorigsäure-chlorid	Dialkyl phosphorochloridite	Dialkoxy-chloro-phosphine
Phosphorigsäure-alkylester-clhorid-dialkylamid	Alkyl dialkylphosphoramido-chloridite	Dialkylamino-alkoxy-chloro-phosphine
Phosphorigsäure-alkylester-alkylimid	Alkyl alkylphosphenimidite	Alkylimino-alkoxy-phosphine
Tetralkylphosphonium chlorid	Tetralkylchlorophosphoran	Tetralkylphosphonium chloride
Trialkylphosphinoxyd	Trialkylphosphine oxide	Trialkyl-phosphine oxide
Trialkylphosphin-alkylimid	Trialkyl-alkylphosphinimide	Trialkyl-phosphine-alkylimide
Alkylphosphonsäure	Alkylphosphonic acid	Alkyl-dihydroxy-phosphine oxide
Alkylphosphonsäure-dialkylester	Dialkyl alkylphosphonate	Dialkoxy-alkyl-phosphine oxide
Alkylphosphonsäure-alkylester-chlorid	Alkyl alkylphosphonochloridate	Alkoxy-alkyl-chloro-phosphine oxide or alkoxy-alkyl-phosphoryl chloride
Alkylphosphonsäure-dichlorid	Alkylphosphonic dichloride	Alkyl-dichloro-phosphine oxide or alkyl-phosphoryl dichloride
Alkylphosphonsäure-alkylester-dialkylamid	Alkyl-alkyl-dialkylphosphon-amidate	Dialkylamino-alkoxy-alkyl-phosphine oxide
Alkylphosphonsäure-chlorid-dialkylamid	Alkyl-dialkylphosphonamidic chloride	Dialkylamino-alkyl-chloro-phosphine oxide or dialkylamido-alkyl-phosphoryl chloride
Alkylphosphonsäure-dialkyl-ester-alkylimid	Dialkyl alkyl-alkylphosphon-imidate	Dialkoxy-alkyl-phosphine-alkylimide
Alkylphosphinigsäure	Alkylphosphinic acid	Alkyl-hydroxy-phosphine oxide
Dialkylphosphinigsäure	Dialkylphosphinic acid	Dialkyl-hydroxy-phosphine oxide
Dialkylphosphinigsäure-alkyl-ester	Alkyl dialkylphosphinate	Alkoxy-dialkyl-phosphine oxide
Dialkylphosphinigsäure-chlorid	Dialkylphosphinic chloride	Dialkyl-chloro-phosphine oxide or dialkyl-phosphoryl chloride

Continued Table 1.

Formula	Present name in		
	USA I [4]	USA II [5]	Britain
$R_2PO(NR_2)$	Dialkyl-dialkylphosphinic amide	Dialkyl-dialkylphosphone amide	Dialkyl-dialkylaminophosphine oxide[6]
$R_2(RO)P=NR$	Alkyl alkylimidodialkylphosphinate	Alkyl alkylimidodialkylphosphonate	—
$(RO)_3PO$	Trialkyl phosphate	Trialkyl phosphate	Trialkyl phosphate
$(RO)_2POCl$	Dialkyl chlorophosphate	Dialkyl chlorophosphate	Dialkyl chlorophosphonate
$(RO)_2(R_2N)PO$	Dialkyl dialkylamidophosphate	Dialkyl dialkylamidophosphate	—
$(RO)(R_2N)POCl$	Alkyl dialkylamidochlorophosphate	Alkyl chlorodialkylamidophosphate	—
$(R_2N)POCl_2$	Dialkylamidophosphoric dichloride	Dichlorodialkylamidophosphate	Dichlorodialkylaminophosphine oxide
$(RO)_3P=NR$	Trialkyl alkylimidophosphate	Trialkyl alkylimidophosphate	—

proposed in Ergwk. are included in the table in cases where Hptwk. and Ergwk. have different nomenclatures. Furthermore, the new Anglo-American proposals [7] are incorporated in the table.

In attempting a systematic designation of organic phosphorus compounds containing one phosphorus atom, acids of phosphorus have generally been taken as a basis. Consequently the following eight acids, regardless of whether they exist as such or not, have to be employed:

$(HO)_3P$	$(HO)_3PO$
$HP(OH)_2$	$HPO(OH)_2$
$H_2P(OH)$	$H_2PO(OH)$
$(HO)PO$	$(HO)PO_2$

These acids, however, do not cover all possibilities, and it has been necessary to designate the remaining compounds as derivatives of the following hydrides:

$$H_3P \qquad H_3PO \qquad H_5P$$

The possibility also exists of basing a nomenclature entirely on the last three compounds, as was already attempted by Michaelis [1], whose nomenclature unfortunately never gained universal recognition. This principle is to be preferred, because so many substituents have been introduced into some compounds that they can scarcely be regarded as derivatives of phosphorus acids.

The naming of the above-mentioned acids has already led to considerable confusion. One example is that compounds of the structure $XPO(OR)_2$, where X = *halogen*, and R = *alkyl* or *aryl*, have in the U.S.A. been named *phosphates* but in Britain *phosphonates*. The reason for this is that the British nomenclature has extended *phosphonic acids* to include compounds symbolized

Continued Table 1.

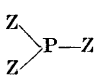
Present name in	Suggested name in	
Germany [6]	USA and Britain [7]	Sweden
Dialkylphosphinigsäure-dialkyl-amid	Dialkyl-dialkylphosphinic amide	Dialkylamino-dialkyl-phosphine oxide
Dialkylphosphinigsäure-alkyl-ester-alkylimid	Alkyl dialkyl-alkylphosphin-imidate	Alkoxy-dialkyl-phosphine-alkyl-imide
Trialkylphosphat	Trialkylphosphate	Trialkoxy-phosphine oxide or trialkyl phosphate
Phosphorsäure-dialkylester-chlorid	Dialkyl phosphorochloridate	Dialkoxy-chloro-phosphine oxide or dialkoxy-phosphoryl chloride
Phosphorsäure-dialkylester-dialkylamid	Dialkyl dialkylphosphoramidate	Dialkylamino-dialkoxy-phosphine oxide
Phosphorsäure-alkylester-chlorid-dialkylamid	Alkyl dialkylphosphoramido-chloridate	Dialkylamino-alkoxy-chloro-phosphine oxide or dialkylamido-alkoxy-phosphoryl chloride
Phosphorsäure-dichlorid-dialkyl-amid	Dialkylphosphoramidic di-chloride	Dialkylamino-dichloro-phosphine oxide or dialkylamido-phosphoryl dichloride
Phosphorsäure-trialkylester-alkylimid	Trialkyl phosphorimidate	Trialkoxy-phosphine-alkylimide

by $XPO(OH)_2$ and not limited the term to compounds of the structure $RPO(OH)_2$, as in the American nomenclature. A much more serious discrepancy is demonstrated by the use of the two acids $R_2PO(OH)$ and $RP(OH)_2$. In the American nomenclature *phosphinic acid* has been used for the former whereas the same name has been used for the second one in the British nomenclature; the British designation for the first acid has been *phosphonous acid*, which in the U.S.A. has been used for the second acid. The German nomenclature in general adheres to the use of names derived from corresponding acids, but is not consistent.

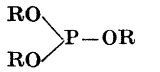
The nomenclature recently proposed in Britain and the U.S.A. [7] by the Organic Division's Advisory Committee on the Nomenclature of Organic Phosphorus Compounds constitutes an attempt to devise an entirely logical system covering all possibilities and all possible structures, whether existing now or not. In so doing, the committee invented a number of new names and endings, some of which may create further confusion. Quite apart from the linguistic point of view this nomenclature seems to be too perfectionistic, and the great number of endings makes it difficult and, indeed, unpractical.

To avoid the illogicalities apparent in earlier British and American nomenclature, and to exclude new unfamiliar names and endings, we have for several years used our own nomenclature, which has a simple construction and obviates misunderstanding. This nomenclature is set forth in the last column of Table 1. A few very simple rules make it readily comprehensible. Our nomenclature can be set forth according to the following simple principles.

I. All compounds containing tervalent phosphorus of the type



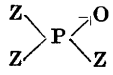
where Z is any univalent radical, are named *phosphines*. If all radicals are linked to phosphorus with oxygenbridges,



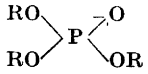
(R = *alkyl* or *aryl*)

the old designation *phosphite* may alternatively be used.

II A. Compounds containing quinquevalent phosphorus of the structure



where Z is any univalent radical, are named *phosphine oxides*. This does not exclude the use of ordinary designations, as *phosphates*, for compounds of the general structure



(R = *alkyl* or *aryl*)

Furthermore, the use of *phosphoryl* is recommended wherever practicable, for example in compounds containing *halide*, *cyanide*, etc., although it does not cover all possibilities. The employment of *phosphoryl* is justified by the common knowledge of that radical and by the ease with which it can be used in designating and pronouncing of a large number of compounds.

II B. The well-known designation of *phosphonium* compounds

$$R_4PX \qquad (R = \textit{alkyl} \text{ or } \textit{aryl} \text{ and } X = \textit{halide} \text{ etc.})$$

has not been considered necessary to change.

Structures formed by the operation of replacing one or two H's in H_3P or H_3PO respectively O in H_3PO are designated by the incorporation of appropriate affixes. The list of affixes is given in Table 2.

Table 1 does not show how compounds in which oxygen is substituted for sulphur, are named. Some authors use *thio* in such cases irrespective of how the sulphur atom is linked, though most of them use *thio* or *thiolo* only for compounds in which sulphur forms a bridge between phosphorus and another atom, whereas compounds with sulphur linked only to phosphorus is named by means of the prefix *thiono*. According to the new Anglo-American nomenclature the location of substituents in esters containing sulphur is denoted by the symbols O- and S-prefixed to the radical name; the symbol S is used in conjunction with the affix *thio*. The affixes *thiolo* and *thiono* are used only where ambiguity arises. Our proposal in this case appears from Table 2.

The radical R_2N- is designated as *dialkylamino* in *phosphines* and *phosphineoxides*, but in compounds denominated with the aid of *phosphoryl* the radical is named *dialkylamido-* to preserve the analogy to the well-known name *phosphoryltriamide*.

As to the order of the various radicals in denoting a compound, we suggest the following: *alkylimino-*, *alkylamino-*, *alkoxy-*, *alkyl-*, *hydroxy-*, *oxo-*, *halo-*

Table 2. List of affixes.

Replacement of	Affix in		
	H_3P	H_3PO According to	
		Phosphine oxide designation	Phosphoryl designation
Two H's by RN=	alkylimino-	alkylimino-	alkylimido-
O by RN=	—	-phosphine-alkylimide	—
H by R_2N-	dialkylamino-	dialkylamino-	dialkylamido-
H by RO-	alkoxy-	alkoxy-	alkoxy-
H by RS-	alkylmercapto-	alkylmercapto-	alkylmercapto-
H by R-	alkyl-	alkyl-	alkyl-
H by HO-	hydroxy-	hydroxy-	hydroxy-
H by HS-	mercapto-	mercapto-	mercapto-
Two H's by O=	oxo-	oxo-	oxo-
O by S=	—	-phosphine sulphide	-thiophosphoryl
H by F-	fluoro-	fluoro-	fluoride
H by Cl-	chloro-	chloro-	chloride
H by Br-	bromo-	bromo-	bromide
H by I-	iodo-	iodo-	iodide
H by NC-	cyano-	cyano-	cyanide
H by NCO-	cyanato-	cyanato-	cyanate

geno-. In Table 2 the radical R is consistently denoted as *alkyl*, but it may of course, also be an aromatic radical, *i. e. aryl*.

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