Pure & Appl. Chem., Vol.55, No.2, pp.409-416, 1983.
Printed in Great Britain.

0033-4545/83/020409-08$03.00/0
Pergamon Press Ltd.

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ORGANIC CHEMISTRY DIVISION

COMMISSION ON NOMENCLATURE OF ORGANIC CHEMISTRY*

REVISION OF THE EXTENDED HANTZSCH-WIDMAN SYSTEM OF NOMENCLATURE FOR HETEROMONOCYCLES

(Recommendations 1982)

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ORGANIC CHEMISTRY DIVISION

Commission on Nomenclature of Organic Chemistry

REVISION OF THE EXTENDED HANTZSCH-WIDMAN SYSTEM OF NOMENCLATURE FOR HETEROMONOCYCLES (see Note a)

(Recommendations 1982)

INTRODUCTION

In 1887 and 1888, Hantzsch (ref. 2) and Widman (ref. 3) independently introduced methods for naming five- and six-membered nitrogen monocycles. Although differing in details, such as expressing the order of the heteroatoms and indicating their positions in the ring, both methods were based on the same underlying principle, i.e., the combination of appropriate prefixes, representing heteroatoms, with stems, representing the size of the ring. At first, only the heteroatoms oxygen, sulfur, and selenium, in addition to nitrogen, and the stems -ol (-ole) and -in (-ine) denoting five- and six-membered rings, respectively, were used. Although these initial proposals underwent the usual discussion, refinement, and inevitable modification, the basic principle survived (ref. 4).

The system was extended to include rings of other sizes, additional heteroatoms, and the expression of various levels of hydrogenation (refs. 5 and 6) and eventually was documented by Patterson and Capell in 1940 as a systematic method for naming heteromonocycles (ref. 7). Stems were provided for all the various levels of hydrogenation for three-, four-, and five-membered rings, but for the six- through ten-membered rings stems were provided only for the completely unsaturated rings and the completely saturated rings without nitrogen atoms. The type of heteroatom to which the system was applicable was apparently not limited; the first edition of The Ring Index (ref. 7) contains examples of heteromonocycles with the metallic heteroatoms Bi, Ge, Sn, Pb, Zn, Hg, and Cu as well as many nonmetallic heteroatoms.

In 1957, the IUPAC Commission on Nomenclature of Organic Chemistry codified this extension of the Hantzsch-Widman system as part of its rules for the nomenclature of organic chemistry (ref. 8a). The heteroatoms to which the system applied were specified and certain exceptions and modifications were noted in order to avoid formation of names identical with some already in use for entirely different compounds.

DISCUSSION

Since the 1957 Rules, the only heteroatom added to the system was boron, first mentioned in a comment to the Rules (ref. 9) and included officially in the third edition of Sections A and B of the Organic Nomenclature Rules (ref. 10a). However, exceptions and modifications to the system were added in both the third edition (ref. 10b) and the fourth edition (ref. 1b) of Sections A and B. The exceptions and modifications all involve six-membered heteromonocycles and are summarized below.

1. Names for saturated six-membered rings without nitrogen, but containing silicon, germanium, tin, or lead, are excluded (ref. 1c) because of names such as silane and disilane for acyclic hydrides (refs. 11 and 12). Although the same problem occurs with the analogous boron rings, they were not excluded; instead the stem "-inane" was used in place of "-ane" (ref. 1d). Although not codified in the IUPAC Organic Nomenclature Rules, this stem change and modified prefixes such as "germana-" rather than "germa-", have been used to avoid this problem with other saturated six-membered rings (refs. 7 and 13).

Note a. These recommendations replace entirely Rule B-1. Extension of the Hantzsch-Widman System, in Section B: Fundamental Heterocyclic Systems, of the IUPAC Rules for Nomenclature of Organic Chemistry (ref. 1a).

2. Names for six-membered rings that contain phosphorus, arsenic, or antimony require a change in the prefix for denoting the heteroatom because of names such as arsine and diphosphine for acyclic hydrides (ref. 1e). These prefix modifications were fully documented for the unsaturated rings in the 1957 Organic Rules (ref. 8b), but their use for saturated rings was noted only in the third edition of the Sections A and B Rules (ref. 10c). Even a modified prefix is not enough for saturated six-membered phosphorus rings; the stem "-inane" instead of "-ane" is also needed to avoid the name phosphorane used for PH_5 (ref. 1d). (See Note a)

In addition to the problems noted above in naming six-membered rings according to the present rules, a number of other comments on the system have been made over the years, including the following:

1. Stems should be provided for saturated rings containing nitrogen with more than six ring members.

2. The system should be extended beyond ten-membered rings.

3. The halogen elements should be included since the system has been applied for naming rings containing cationic halogen ring atoms.

4. Other metallic elements should be included.

5. The numbering rules should be completely consistent with those for numbering heteroatoms in polycyclic ring systems.

CONCLUSIONS

Although the Hantzsch-Widman system for naming heteromonocycles as currently documented (ref. 1a) has some complications and defects, as noted above, it does have distinct advantages and is widely used, not only for naming heteromonocycles, but also for describing heteromonocyclic components in naming fused heterocyclic systems. Therefore, the IUPAC Commission on Nomenclature of Organic Chemistry decided that a revision of the system was justified and would be useful, and prepared provisional recommendations for such a revision (ref. 14). On the basis of the comments received on the provisional recommendations, the Commission now presents the following recommendations. The main points may be summarized briefly as follows:

1. The stems for three-membered rings containing nitrogen and for saturated four and five-membered rings containing nitrogen are retained. The use of the stems "-inine" and "-inane" to name six-membered rings where the stems "-ine" and "-ane" would be ambiguous has been carefully delineated. All other heteromonocycles containing no more than ten ring members are named by a single set of endings for each ring size.

2. The special terminations for four- and five-membered rings containing one double bond when two double bonds are possible (ref. 1f) are no longer recommended.

3. The number of elements covered by the system is increased to nineteen by including the halogen elements needed for naming heterocyclic rings containing halogen ring members.

4. The numbering rules in the present Hantzsch-Widman rules (ref. 1g) are retained.

5. The subtractive prefix "dehydro" (see ref. 15a) is introduced as an alternative to the additive prefix "hydro" (see ref. 15b) for naming unsaturated heteromonocycles having less than the maximum number of noncumulative double bonds.

Note a. In the fourth edition of the Section B Organic Rules (ref. 1a) the prefix for bismuth was changed to bisma-, as it had been in the first and second editions of Section B (refs. 8b and 8c), thus removing the need for an exception for bismuth rings in order to avoid the same problem for six-membered bismuth rings as noted here for the corresponding phosphorus, arsenic, and antimony rings.

RECOMMENDATIONS

The following recommendations, designated in this report as RB (from Revision of the B rules), are a revision of the rules given under Rule B-1 of the 1979 edition of the IUPAC Rules of Nomenclature of Organic Chemistry (ref. 1a) and replace them in their entirety.

This revision is intended to provide a system for naming all heteromonocycles having no more than ten ring members in which the heteroatoms are in defined standard valence states (see Note a).

Obviously the system could easily accommodate all elements, if a defined valence state has been accepted. However, it should be extended only with necessary caution to avoid confusion with existing terminology.

These recommendations are not intended to supersede commonly used trivial names, such as thiophene, furan, pyrrole, pyridine, and morpholine, that are recognized under Rule B-2 (ref. 1h); but do supersede those names for partially saturated heteromonocycles requiring special terminations as given by Rule B-1.2 (ref. 1f).

Heteromonocycles with more than ten ring members are named by replacement nomenclature as described by Rule B-4.1 (ref. 1i).

RB-1.1. (Replaces Rules B-1.1, in part, and B-1.51). A saturated monocycle with no more than five ring members, and having only a single nitrogen atom, is named by adding the prefix "aza-" (see Table I) with elision of the final "a" of the prefix (see Note b) to a stem "-iridine", "-etidine", or "-olidine" according to whether the ring has three, four, or five ring members, respectively. The numbering begins with the nitrogen atom.

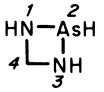
Two or more nitrogen atoms are denoted by appropriate numerical prefixes (see RB-1.3).

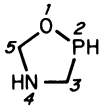
Other heteroatoms in addition to nitrogen atoms are indicated by appropriate prefixes from Table I. The order of citation of the prefixes and the numbering of the heteromonocycle follow the principles in RB-1.4.

Examples:

1.  Aziridine

2.  1,3-Diazetidine

3.  1,3,2-Diazarsetidine

4.  1,4,2-Oxazaphospholidine

Note: This recommendation is not intended to supersede trivial names recognized under Rule B-2 (Ref. 1h), such as pyrrolidine or imidazolidine.

RB-1.2. (Replaces Rules B-1.1, in part, and B-1.51). A monocycle with no more than ten ring members, one of which is a heteroatom given in Table I, is named by combining the appropriate prefix from Table I with a stem from Table II, except as provided by RB-1.1, with elision of the final "a" of the prefix, when followed by a vowel (see Note b).

Note a. A defined valence state is required for the unambiguous application of the principle of maximum number of noncumulative double bonds.

Note b. In organic replacement nomenclature the final "a" of the replacement prefix is not elided (ref. 15c).

TABLE I: PREFIXES FOR THE HANTZSCH-WIDMAN SYSTEM (see Note a)

Element	Valence	Prefix	Element	Valence	Prefix
Fluorine	I	Fluora	Arsenic	III	Arsa
Chlorine	I	Chlora	Antimony	III	Stiba
Bromine	I	Broma	Bismuth	III	Bisma
Iodine	I	Ioda	Silicon	IV	Sila
Oxygen	II	Oxa	Germanium	IV	Germa
Sulfur	II	Thia	Tin	IV	Stanna
Selenium	II	Selena	Lead	IV	Plumba
Tellurium	II	Tellura	Boron	III	Bora
Nitrogen	III	Aza	Mercury	II	Mercura
Phosphorus	III	Phospha			

TABLE II. STEMS FOR THE HANTZSCH-WIDMAN SYSTEM (see Notes b, c, and d)

The stem for six-membered rings depends on the least preferred heteroatom in the ring (see RB-1.4), i.e., the heteroatom whose name directly precedes the stem.

To determine the proper stem for six-membered rings, select the set below that contains the least preferred heteroatom before consulting the table. For example, the proper stem for the dioxazine ring is found after set 6B, which contains the element nitrogen.

6A O[1], S, Se, Te, Bi, Hg
6B N[2], Si, Ge, Sn, Pb
6C B, F, Cl, Br, I, P, As, Sb

Ring Size	Unsaturated[3]	Saturated[4]	Ring Size	Unsaturated[3]	Saturated[4]
3	irene[5]	irane[6]	7	epine	epane
4	ete	etane[6]	8	ocine	ocane
5	ole	olane[6]	9	onine	onane
6A	ine[1]	ane	10	ecine	ecane
6B	ine[2]	inane			
6C	inine	inane			

(1) Oxine should not be used for pyran because it is used as a trivial name for 8-quinolinol.

(2) Azine cannot be used for pyridine because of its long established use as a class name for =N-N= compounds (ref. 15d).

(3) Used when the ring contains the maximum number of noncumulative double bonds and at least one double bond is present when the heteroatoms have the valences given in Table I (see also Note 4).

(4) Used when no double bonds are present or when none are possible.

(5) The traditional stem "irine" may be used for rings containing nitrogen only.

(6) The traditional stems "iridine", "etidine", and "olidine" are preferred for rings containing nitrogen and are codified in RB-1.1.

Note a. Prefixes for the halogen elements are included in order to provide for naming heteromonocycles containing cationic halogen atoms (to be described in a later report) and halogen atoms in nonstandard valence states (ref. 17).

Note b. A terminal "e" is used on all stems in these recommendations but is optional.

Note c. The stems for ring sizes 3, 4, 7, 8, 9, and 10 may be considered to be derived from numerical prefixes as follows: "ir" from tri, "et" from tetra, "ep" from hepta, "oc" from octa, "on" from nona, and "ec" from deca.

Note d. The stems "etine" and "oline", which would be consistent with the other stems for unsaturated rings, cannot be used because they were formerly used to name four- and five-membered rings containing nitrogen, respectively, having only one of two possible double bonds (ref. 1f).

The presence of at least one hydrogen atom on a ring atom joined to adjacent ring atoms by only single bonds in an unsaturated monocycle containing the maximum number of noncumulative double bonds is denoted by the technique used for indicated hydrogen (see examples 2 and 4 below) (ref. 16).

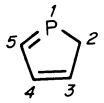
The numbering of the heterocycle begins with the heteroatom. Thereafter indicated hydrogen takes precedence for low locants.

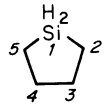
Examples:

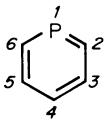
1.  Oxirane

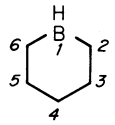
2.  1H-Azirene
1H-Azirine (traditional)

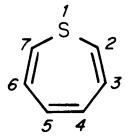
3.  Azete

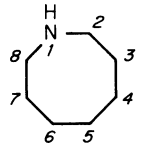
4.  2H-Phosphole

5.  Silolane

6.  Phosphinine
(formerly Phosphorin)

7.  Borinane

8.  Thiepine

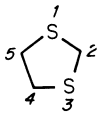
9.  Azocane
(formerly Octahydroazocine)

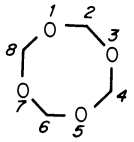
RB-1.3. (Replaces Rules B-1.3 and B-1.52). Two or more heteroatoms of the same element in a heteromonocycle are indicated by adding an appropriate numerical prefix, such as "di", "tri", etc., to the prefix for the heteroatom (Table I). A final "a" of a numerical prefix is elided when followed by a vowel.

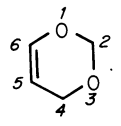
The positions of the heteroatoms are given by numerical locants cited in front of the name. Numbering begins at a heteroatom and proceeds in the direction that gives the lowest set of locants to the heteroatoms (see Note a).

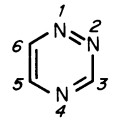
Note: Designation of hydrogen atoms by the technique of indicated hydrogen (see RB-1.2) at ring positions between two bivalent ring atoms may be omitted.

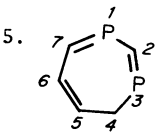
Examples:

1.  1,3-Dithiolane
(the locant set 1,3 is lower than 1,4)

2.  1,3,5,7-Tetroxocane

3.  2H,4H-1,3-Dioxine
(may be written as 4H-1,3-Dioxine; indication of the hydrogen atom at position 2 may be omitted as explained in the Note to this rule)

4.  1,2,4-Triazine
(the locant set 1,2,4 is lower than 1,2,5; 1,3,4; or 1,4,5)

5.  4H-1,3-Diphosphepine
(heteroatoms are preferred to indicated hydrogen for lowest locants)

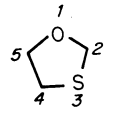
Note a. The lowest set of locants is that series which contains the lowest number at the first point of difference when two or more series containing the same number of terms are compared term by term (ref. 15e).

RB-1.4. (Replaces Rules B-1.4 and B-1.53). A heteromonocycle with two or more different heteroatoms is named by adding the appropriate prefix for each heteroatom (Table I) together with a numerical prefix as prescribed by RB-1.3 if needed, in the order of appearance of the heteroatoms in Table I (see Note a) to an appropriate stem (RB-1.1 or RB-1.2). The final "a" of a numerical prefix is elided when followed by a vowel.

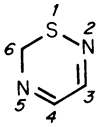
The positions of the heteroatoms are indicated by numerical locants, all of which are cited before the first heteroatom prefix and in the same order as the heteroatom prefixes to which they refer.

Numbering of the heteromonocycle begins with a heteroatom whose prefix occurs earliest in Table I. If there is any choice, the numbering should give the lowest set of locants (see Note a to Rule RB-1.3) first to all heteroatoms, then to heteroatoms in the order of their prefixes.

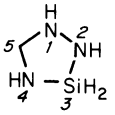
Examples:

1. 

1,3-Oxathiolane
(the locant set 1,3 is lower than 1,4)

2. 

6H-1,2,5-Thiadiazine (preferred)
(the numbering begins with the sulfur atom, and then the locant set 1,2,5 is lower than 1,3,6)

3. 

1,2,4,3-Triazasilolidine

Note that numbering beginning with either nitrogen atom adjacent to the single carbon atom results in the same lowest locant set, 1,2,3,4, for the four heteroatoms taken as a complete set without regard to priority. The direction for numbering thus depends on the comparison of these two locant sets in the order that the heteroatoms to which they refer are cited, namely, 1,3,4,2 and 1,2,4,3; the latter set has the lower second locant and is therefore preferred.

RB-1.5. (Replaces Rule B-1.2) (see Note b). A heteromonocycle containing fewer than the maximum number of noncumulative double bonds may be named by: (a) adding the prefixes "dihydro", "tetrahydro", etc., to a parent name that indicates the presence of the maximum number of noncumulative double bonds; or (b) adding the prefixes "didehydro", "tetradehydro", etc., to a parent name that indicates a fully saturated structure, according to the requirements of Rules C-16.1 and C-41.2 (ref. 15f). **Method (a) is usually preferred.**

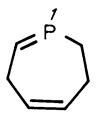
Heteroatoms and indicated hydrogen have preference over hydro and dehydro prefixes for determining the beginning and direction of numbering.

Note: The final "o" of a hydro or dehydro prefix is not elided before a following vowel.

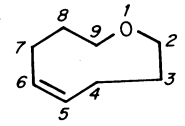
Examples:

1. 

(a) 1,2-Dihydroazete
(b) 2,3-Didehydroazetidine
(formerly Δ^2-Azetine or 2-Azetine)

2. 

(a) 3,6-Dihydro-2H-phosphepine
(b) 1,2,4,5-Tetradehydrophosphepane

3. 

(a) 2,3,4,7,8,9-Hexahydrooxonine
(b) 5,6-Didehydrooxonane

Note a. This order of citation follows the element sequence now accepted in the rules of both inorganic (ref. 18) and organic (ref. 19) nomenclature.

Note b. Thus, the special terminations for partially saturated heteromonocycles as given by Rule B-1.2 (ref. 1f) are no longer recommended.

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