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PROVISIONAL

INTERNATIONAL UNION OF PURE
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ORGANIC CHEMISTRY DIVISION

COMMISSION ON NOMENCLATURE OF ORGANIC CHEMISTRY*

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

(IUPAC Nomenclature of Organic Chemistry, Section B:
Fundamental Heterocyclic Systems, Rule B-1.
Extension of the Hantzsch-Widman System)

(Provisional Recommendations, 1978)

Comments on these recommendations should be sent within 8 months of publication to the Secretary of the Commission:

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Comments from the viewpoint of languages other than English are especially encouraged. These may have special significance regarding the publication in various countries of translations of the nomenclature eventually approved by IUPAC.

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NOMENCLATURE OF ORGANIC CHEMISTRY

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

(Provisional Recommendations, 1978)

INTRODUCTION

In 1887 and 1888, Hantzsch (Ref. 1) and Widman (Ref. 2) independently introduced methods for the nomenclature of nitrogenous five- and six-membered heteromonocycles. Although differing in details such as the expression of the order of the heteroatoms and methods for 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. 3).

The system was extended to include rings of other sizes, additional heteroatoms, and the expression of various levels of hydrogenation (Refs. 4 & 5); and eventually documented by Patterson and Capell in 1940 as a systematic method for naming heteromonocycles (Ref. 6). Stems were provided for all of the various levels of hydrogenation for the 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 not containing nitrogen. The type of heteroatom to which the system was to be applied was apparently not limited; the first edition of the Ring Index (Ref. 6) contains examples of heteromonocycles with the metallic heteroatoms Bi, Ge, Sn, Pb, Zn, Hg, and Cu, as well as many of the nonmetallic elements.

DISCUSSION

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. 7). The heteroatoms to which the system applied were specified and certain exceptions and modifications were noted in order to avoid the generation of names identical to some already being used for entirely different compounds. Although not documented in the 1957 Rules, the use of boron as a heteroatom in the system was recognized in a comment to these Rules (Ref. 8) and subsequently included in the third edition of the Section A and B Rules (Ref. 9a).

The exceptions and modifications that were necessary all involved the stems for six-membered rings. These are summarized below.

1. Names for the saturated six-membered rings without nitrogen but containing Si, Ge, Sn, Pb were excluded (Ref. 9c) because names such as silane (SiH_4) and digermane ($H_3Ge\text{-}GeH_3$) were in use for acyclic hydrides. Although never codified in Section B of the IUPAC Organic Nomenclature Rules, modified prefixes and stems were used to avoid conflicts with acyclic hydride names in the compilation of ring names by the American Chemical Society (Ref. 10); the prefix germana- was used in place of germa- and the stem -inane was used instead of -ane (Ref. 6).

Note a. When eventually approved, this revision will replace, in its entirety, Rule B-1. Extensions of the Hantzsch-Widman System, in Section B: Fundamental Heterocyclic Systems of the IUPAC Rules for the Nomenclature of Organic Chemistry (Ref. 9b).

2. The names for the unsaturated six-membered rings containing P, As, or Sb required a change in the prefix for denoting the heteroatom (Ref. 9d) because names such as arsine (AsH_3) and diphosphine (H_2P-PH_2) were in use for the acyclic hydrides. Although not fully documented in Section B of the IUPAC Organic Nomenclature Rules, these changes in the prefixes were also carried over to the analogous saturated rings; this was noted in the third edition of the Section B rules only for the arsenic prefix. For saturated six-membered phosphorus rings even the modified prefix was not enough; the -inane stem modification noted in 1., above, was also needed and this was recognized in the third edition of the Section B rules (Ref. 9e).

3. Prior to the appearance of the third edition of Section B of the IUPAC Organic Nomenclature Rules, no special provisions were needed for rings containing bismuth atoms. However, in the third edition of the Section B rules, the prefix for the element bismuth was changes from bisma to bismutha (Ref. 9a) resulting in the same problem with the name of the acyclic hydride bismuthine as noted in 2., above, for the elements phosphorus, arsenic, and antimony.

In addition to the problems noted above in naming six-membered rings according to the present rules, a number of other criticisms of the system have been made over the years, as summarized below.

1. Stems for saturated nitrogenous rings with more than five ring members are not provided.

2. The halogen elements are not included but the system is used to name rings containing cationic halogen atoms, e.g., bromolium (Ref. 10).

3. The rules for numbering the heteroatoms are not consistent with those for numbering heteroatoms in polycyclic systems.

CONCLUSIONS

Although the Hantzsch-Widman system for naming heteromonocycles as currently documented has a number of complications and minor defects, as is evident from the above discussion, it does have advantages and is widely used in fusion nomenclature to describe heteromonocyclic components of fused-ring systems. Therefore, the IUPAC Commission on Nomenclature of Organic Chemistry feels that a revision of the system is justified and proposes the revised rules as given in this document. The major changes proposed are summarized briefly as follows:

1. The stems for saturated nitrogenous rings and for unsaturated rings without nitrogen are eliminated and the remaining set of stems is applied to rings whether or not they contain nitrogen. Because there is no longer a strong feeling that nitrogenous rings need to be distinguished in systematic organic nomenclature from those without nitrogen, there is not sufficient need for retaining two separate sets of stems.

2. The special terminations used for four- and five-membered rings containing one double bond when there can be more than one double bond (Ref. 9f) are discontinued.

3. The number of elements covered by the system is increased to 19 by including the halogen elements that are needed for naming rings containing cationic halogen atoms.

4. The requirement that the numbering of a heteromonocycle begins with a heteroatom has been retained, but the requirement that this heteroatom be one of highest priority has been dropped. Thus, the numbering of heteroatoms in heteromonocycles named by the Hantzsch-Widman system follows the same rules as for fused-heteropolycyclic systems (Ref. 9g).

5. The new stems -ixine and -ixane (see Note a.), derived from the English word "six", are introduced replacing -in (-ine) and -ane (-inane) for six-membered rings to avoid the problems noted above. It should be noted that the extension of the "-inane" stem modification (Ref. 6) already used for a number of saturated six-membered rings would not eliminate the need for modified element prefixes as given in Table I of Rule B-1.1 (Ref. 9a); and the extension of prefix modifications already in use does not seem justifiable. The adoption of the proposed new stems for the six-membered rings eliminates the need for any prefix changes.

RULES

When eventually approved, the following rules will constitute a revision of the present rules as described in Rule B-1 of the IUPAC Organic Nomenclature Rules (Ref. 9b).

This revision is intended to provide a system for naming all heteromonocycles having no more than ten ring atoms and in which the heteroatoms are mainly nonmetallic. The metallic heteroatoms bismuth, germanium, tin, lead, and mercury are included because of previous usage. However, even though the system can easily accommodate all of the other elements, its extension to other elements should be made with considerable caution because there is the possibility of confusion with present terminology and because of the problem of variable valency, especially with the transition metals.

These rules are <u>not</u> intended to prohibit the use of commonly used trivial names, such as thiophene, pyran, pyridine, and morpholine, given under Rule B-2 (Ref. 9h). Heteromonocycles with more than ten ring members are named by replacement nomenclature as described by Rule B-4.1 (Ref. 9i) except that the priorities for numbering the heteroatoms should follow the principles in this revision as given below.

RULE RB-1.1 (Replaces B-1.1 and B-1.51). A monocycle having 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, eliding a final "a" of a prefix before a following vowel (see Note b.).

TABLE I

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			

NOTE: The halogens are included in order to be able to provide names for monocycles containing cationic halogen atoms.

Note a. These stems were chosen in preference to "-exine" and "-exane" because of the close similarity with "-hexane" which might be indistinguishable in speech.

Note b. Note that this contrasts with organic replacement nomenclature in which such vowels are not elided (Ref. 9j).

TABLE II

Ring Size	Unsaturated	Saturated	Ring Size	Unsaturated	Saturated
3	irine	irane	7	epine	epane
4	ete	etane	8	ocine	ocane
5	ole	olane	9	onine	onane
6	ixine	ixane	10	ecine	ecane

NOTES: (1) The stems denoting ring size may be considered to be derived from numerical prefixes or number words as follows "ir" from tri, "et" from tetra, "ix" from six, "ep" from hepta, "oc" from octa, "on" from nona, "ec" from deca.

(2) The stem "etine", which would be consistent with the other stems denoting unsaturation, cannot be used because it was formerly used to denote a four-membered nitrogenous ring containing only one of two possible double bonds (Ref. 9f).

(3) When the final "e" of the stem "-ole" is dropped, as will occur in some languages, the result is a name ending in -ol. This ending must not be taken to indicate the presence of a hydroxy group; the latter must be separately indicated, as 1,3-Selenazol-2-ol.

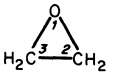
(4) The stems "-ixine" and "-ixane" were chosen in preference to "-exine" and "-exane" because of the close similarity with "-hexane", which might be indistinguishable in speech.

The stems denoting saturation are applicable when no double bonds are present or possible.

The stems denoting unsaturation are applicable when at least one double bond is present and the ring contains the maximum number of noncumulative double bonds when the heteroatoms have the valencies as given in Table I. The presence of hydrogen atoms at an isolated, saturated ring atom of an unsaturated monocycle is denoted by the "indicated hydrogen" method (Ref. 9k), even when the saturated ring atom is flanked by only bivalent ring atoms.

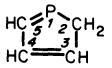
Numbering of a heteromonocycle must begin with a heteroatom; thus, heteroatoms are preferred to indicated hydrogen for the assignment of lowest locants.

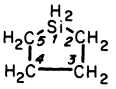
Examples:

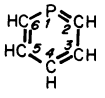
1.  Oxirane

2.  1H-Azirine

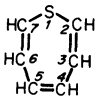
3.  Azete

4.  2H-Phosphole

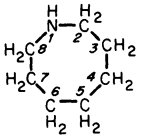
5.  Silolane

6.  Phosphixine (formerly Phosphorin)

Examples (cont.):

7. 

Thiepine

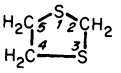
8. 

Azocane

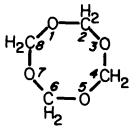
RULE RB-1.2 (Replaces B-1.3 and B-1.52). Multiplicity of the same heteroatom in a heteromonocycle is indicated by the appropriate multiplicative prefix "di-", "tri-", etc., placed directly before the prefix for the appropriate heteroatom from Table I (Rule RB-1.1). A final "a" of a multiplicative prefix is elided when followed by a vowel.

The positions of the heteroatoms are given by numerical locants denoting the numbering of the heteromonocycle and are cited in front of the name. Numbering must begin at a heteroatom and proceed in the direction that will give to the heteroatoms the lowest set of numbers as defined in the footnote to Rule A-2.6(c) (Ref. 9ℓ).

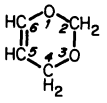
Examples:

1. 

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

2. 

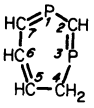
1,3,5,7-Tetroxocane

3. 

2H,4H-1,3-Dioxixine

4. 

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

5. 

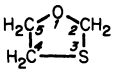
4H-1,3-Diphosphepine (heteroatoms are preferred to indicated hydrogen for lowest locants)

RULE RB-1.3 (Replaces B-1.4 and B-1.53). A heteromonocycle containing two or more different heteroatoms is named by citing the appropriate prefixes, together with numerical prefixes, if required, in the order of their appearance in Table I (Rule RB-1.1) (see Note a.).

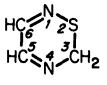
The positions of the heteroatoms are indicated by numerical locants, all of which are cited before the first prefix and in the same order as the citation of the prefixes to which they refer.

Numbering must begin at a heteroatom and proceed in the direction that will give the lowest set of numbers, as defined in the footnote to Rule A-2.6(c) (Ref. 9ℓ), first to all heteroatoms as a complete set without regard to priority and then to the heteroatoms in order of their appearance in Table I (Rule RB-1.1).

Examples:

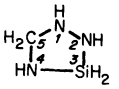
1. 

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

2. 

3H-2,1,4-Thiadiazixine (previously 6H-1,2,5-Thiadiazine) (the locant set 1,2,4 is lower than the locant set 1,2,5; 1,3,4; or 1,4,5)

NOTE: The previous set of rules required the numbering to begin at a preferred heteroatom (Ref. 9m); thus the locant "1" was assigned to the first cited heteroatom, the sulfur atom in the example 2.

3. 

1,2,4,3-Triazasilolane

NOTE: Numbering of the above heteromonocycle starting with either of the nitrogen atoms adjacent to the carbon atom results in the same lowest locant set, 1,2,3,4, for the four heteroatoms as a complete set without regard to priority (Ref. 9ℓ).

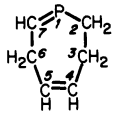
The choice between the two names, 1,3,4,2-triazasilolane and 1,2,4,3-triazasilolane, is made according to procedures given in the Section C Rules (Ref. 9n), i.e., by comparing these locants in the order of citation in the name, and, because the locant set 1,2,4,3 is lower than the set 1,3,4,2, the name 1,2,4,3-triazasilolane is preferred.

RULE RB-1.4 (Replaces B-1.2). A heteromonocycle whose unsaturation is less than that corresponding to the maximum number of noncumulative double bonds is named by means of hydro prefixes, e.g., "dihydro-", "tetrahydro-", etc., cited in front of the name of the heteromonocycle formed according to Rules RB-1.1, RB-1.2, and RB-1.3, above, according to the requirements of Rule C-16.1 (Ref. 9o). The heteroatom(s) and indicated hydrogen have preference over the hydro prefixes in the determination of the beginning and direction of numbering.

Note a. This order follows the element sequence now accepted in the rules of both inorganic (Ref. 11) and organic nomenclature (Ref. 12).

Examples:

1.  1,2-Dihydroazete (formerly Δ^2-Azetine or 2-Azetine)

2.  3,6-Dihydro-2H-phosphepine (indicated hydrogen is preferred to hydro prefixes for low locants)

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3. See, for example, "Handbuch der Organischen Chemie von Dr. F. Beilstein", 3rd ed., Vol. 4, Leopold Voss, Hamburg and Leipzig, 1899, pp. 1-2.

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7. IUPAC, "Nomenclature of Organic Chemistry (1957)", Sections A and B, 1st ed., Butterworths, London, 1958, Rule B-1, pp. 51-53.

8. IUPAC, "Definitive Rules for Nomenclature of Organic Chemistry", J. Am. Chem. Soc., 82, 5545-5574 (1960).

9. IUPAC, "Nomenclature of Organic Chemistry (1969)", Sections A and B, 3rd ed., (combined with Section C, 2nd ed.), Butterworths, London, 1971: [a] Rule B-1, Table I, p. 53; [b] pp. 53-55; [c] Rule B-1, Table II, footnote (d), p. 53; [d] Rule B-1, Table I, footnote and Table II, footnote (b), p. 53; [e] Rule B-1, Table I, footnote, p. 53; [f] Rule B-1.2, p. 54; [g] Rule B-3.4, p. 66 and Rule B-4.2, p. 68; [h] pp. 55-63; [i] p. 68; [j] p. 83; [k] Rule A-21.6, p. 25; [ℓ] pp. 10-11; [m] Rule B-1.53, p. 55; [n] Rule C-13.11(k), p. 100, and Rule C-14.11(m), p. 105; [o] p. 108.

10. A. M. Patterson, L. T. Capell, and D. F. Walker, "The Ring Index", 2nd ed., American Chemical Society, Washington, D.C., 1960; Supplement I, 1963; Supplement II, 1964; Supplement III, 1965.

11. IUPAC, "Nomenclature of Inorganic Chemistry (1970)", 2nd ed., Butterworths, London, 1971, Table IV, p. 104.

12. IUPAC, "Nomenclature of Organic Chemistry, Section D (Tentative)", IUPAC Information Bulletin Appendices on Tentative Nomenclature, Symbols, Units, and Standards, No. 31, August, 1973, Appendix, Table I, pp. 137-138.