Rules for I.U.P.A.C. Notation for Organic Compounds

International Union of Pure and Applied Chemistry

RULES FOR I.U.P.A.C. NOTATION FOR ORGANIC COMPOUNDS

Issued by the Commission on Codification, Ciphering and Punched Card Techniques

Longmans

Introduction

In October 1946 Dyson[1] suggested a method ('ciphering' or 'cipher notation') by which organic structures were written in linear form independently of nomenclature. The system was based on the principle of dividing the structure into individual rings, chains, functional groups, substituents, etc., and citing these portions in a fixed order by conventional symbols. The system embodied a new mode of numbering the atoms of organic structures, part of which (that dealing with polycyclic systems) was related to a system of numbering independently published by Taylor[2] in 1948; at the suggestion of the late Dr. A. M. Patterson[3] these two systems were reconciled in the I.U.P.A.C. notation.

Other systems of classification and ciphering have since been published; those of van Weerden,[4] Wiselogle[5] and the Chemical-Biological Co-ordination Center[6] are classifications and do not attempt to delineate the complete structural details; those of Gruber[7] and Silk[8] are closely related to the Dyson system; the Gordon–Kendall–Davidson method[9] and that of Wiswesser[10] are based on an approach to the problem fundamentally different from that of Dyson; the Newcastle system[11] is a kind of shorthand for systematic names; Crane and Berry[12] have attempted to combine the Dyson and Wiswesser systems in a notation partly based on a redundancy principle (compare Ref. 13).

In 1947 I.U.P.A.C. appointed a Commission on Codification, Ciphering, and Punched Card Techniques to examine and report upon the various proposals then extant for ciphering organic structures.[14] In 1949 the Commission laid down the following desiderata for an internationally acceptable form of cipher notation. The desiderata are not necessarily in order of relative importance:

1. Simplicity of use.
2. Ease of printing and typewriting.
3. Conciseness.
4. Recognizability.
5. Ability to generate a unique chemical nomenclature.
6. Compatibility with the accepted practices of inorganic chemical nomenclature.
7. Uniqueness.
8. Generation of an unambiguous and useful enumeration pattern.
9. Ease of manipulation by machine methods, for example, by punched cards.
10. Exhibition of associations (descriptiveness).
11. Ability to deal with partial indeterminates.

In 1951, the I.U.P.A.C. Commission on Codification etc.,[15] recommended the adoption of a provisional international system of notation for organic compounds based on the Dyson system, and suggested that, where possible and compatible, useful features from other systems should be incorporated.

Introduction

In 1958[16] a tentative draft of the International System was printed and submitted to the organizations adherent to the Union. During 1959 the large mass of material submitted by the organizations adherent to the Union, and by others, was considered by the Commission, and, where desirable, changes were made.

The thanks of the Commission are extended to the following for their practical contributions to the report at this stage: Professor S. J. Angyal, Australia; Dr. A. Feldman, U.S.A.; Dr. R. Fugmann, Germany; Professor S. Gronowitz, Sweden; Dr. W. Gruber, Germany; Dr. K. Hirayama, Japan; Professor H. Kaiser, Germany; Dr. A. A. Levi, Gt. Britain; Dr. M. F. Ravely, U.S.A.; Dr. J. A. Silk, Gt. Britain; Professor M. L. Wolfrom, U.S.A.

The Commission has taken the view that the systematics of notation should be studied first, and that the uses and applications by machine methods to problems of chemical documentation should form a later part of the work of the Commission. Nevertheless, it has always been kept in mind, during the design and development of this system, that it will be used in indexes, information systems, lexicons of organic chemical data, and in machine systems for correlating the properties of compounds with fractional structural characteristics. This view has led to a simplicity in the use of symbols such that ciphers can be directly punched in, for example, an I.B.M. card and the data retrieved exactly as originally written, with the I.B.M. document–writing machine[17]. The advantages of this notation (apart from machine use) lie in uniqueness, brevity, and ability to give a reasonable degree of classification in indexing; a structure can have only one cipher and this seldom uses more than 30 per cent. of the number of symbols in the systematic name. Another advantage is that the notation can be applied easily to structures for which systematic names cannot be made from existing rules. In addition, the notation substantially complies with the desiderata (see p. vii) which the Commission in its original sessions laid down as essential.

The Commission considers that it has now completed that part of its task which is concerned with the formulation of a satisfactory and workable notation system for organic compounds. This report constitutes the approved International System of Notation for Organic Compounds as issued by I.U.P.A.C. for general use.

Since the inception of the Commission in 1947 the following have served as members: W. Baker*, C. L. Bernier*, H. V. A. Briscoe, R. S. Cahn*, G. M. Dyson*, D. H. Hey, W. R. Kirner, N. Lozac'h*, A. D. Mitchell, H. S. Nutting*, J. W. Perry*, F. Richter*, and P. E. Verkade (*President*)*.

* Present members of the Commission (1960).

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14. *Comptes rendus de la 14me Conférence, I.U.P.A.C.*, 1947, 64; *ibid*, *15me Conférence*, 1949, 64; *ibid*. *16me Conférence*, 1951, 104; *ibid*. *18me Conférence*, 1955, 184.
15. *Comptes rendus de la 16me Conférence*, I.U.P.A.C., 1951, 104.
16. *A Proposed International Chemical Notation*, prepared by the Commission on Codification, Ciphering and Punched Card Techniques of I.U.P.A.C., Longmans, London, 1958.
17. Dyson, G. M. and Riley, E. F., *Chemical and Engineering News*, 1961. **39**, 72.

CONTENTS

SECTION 1

Symbols

THE symbols used for this notation comprise the letters of the alphabet, arabic numerals, and some of the common marks of punctuation. They are:

1.1 *The accepted symbols for the elements* agreed by I.U.P.A.C., with the following exceptions:

1.11 Bo is used for boron since, in this notation, B is used in a structural sense.

1.12 Ch is used for chlorine to avoid confusion between '1' (unity) and 'l' (12th letter of the alphabet). *Note.* Although on some typewriters and in printing a difference can be made between 'Cl35' and 'Cl35' it is often insufficient for a rapid distinction to be made.

1.13 Yt is used for yttrium, since, in this notation, Y is used to denote a triple bond.

1.14 Q is used for (*a*) shared oxygen, that is, an oxygen atom linked to two atoms as in a hydroxyl group or ether, and (*b*) in the compound symbol EQ for oxygen doubly bound in the carbonyl group >C=O (see p. 12, Rule 3.1).

1.2 *Capital letters* are used as follows:

A for a saturated ring system, as in A6, cyclohexane (see p. 41).

B for a ring system with the maximum number of non-cumulative double bonds, as in B6, benzene (see p. 43).

D, *L*, *R* and *S* for stereochemical purposes (see Rule 10.52). These are printed in italics.

E for a double bond (see p. 8).

M for a macrocycle ciphered by assembly notation (see Rule 8.9, p. 70).

O for unshared oxygen as in NO, NO_2, SO, SO_2, IO, IO_2, etc. (see p. 17).

but not for oxygen in >CO and —CHO (see p. 12).

X as in CX for formic acid, or, after the cipher of a parent compound, for a carboxyl group (see p. 13).

Y for a triple bond (see p. 8).

Z to indicate hetero-atoms (see p. 58).

1.3 *Lower-case letters* are used as follows:

a after EQ for aldehydes (see p. 12).

b in a series of locants to indicate the presence of the maximum number of non-cumulative double bonds in a ring (see p. 43).

c and t for *cis-* and *trans-*arrangements at a double bond as in Ec and Et (see p. 73); and for configurational relations in cyclic stereoisomers (see p. 75).

h to designate an implied variable-position hydrogen atom as in B65h8 (see p. 45).

r for stereochemical reference (see p. 75).

x for an unknown number.

1.4 *Punctuation marks and other symbols* are used as follows:

1.41 The *semicolon*; separates the citation of groups attached to the same carbon atom, as in $C_4EQ;N$ for $CH_3CH_2CH_2CO{\cdot}NH_2$ (see p. 17, Rule 3.672) and certain locants in assembly notation (see Rule 4.7412).

1.42 The *colon* : segregates certain locants and components in assembly notation as in $B6_2$:4C/B6 (see p. 23, Rule 4.2).

1.43 *Parentheses* ( ) enclose compound substituents, repetitive components and branch components of assemblies (see pp. 5, 23).

1.44 The stroke / separates components in assemblies. An assembly must contain either a stroke or a colon and may contain both (see pp. 23–35, Rule 4.2 and 4.3).

1.45 *Superscript* $^+$ *and* $^-$ *signs* are used to denote positive and negative charges; double and triple charges are written as in M^{++} and M^{---} (see p. 84).

1.46 *Brackets* [ ] indicate molecular or ionic entities and also the common difference in arithmetical series of locants (see p. 4, Rule 2.45, p. 85, Rules 11.45, and 11.47).

1.47 *Underlining* (*a*) *of letters*, as in NC for the isonitrile group or N_2 for the aliphatic diazo group, denotes the association (without hydrogen) of a group of atoms among which valency relations cannot be simply expressed (see p. 18, Rule 3.674).

(*b*) *of figures* (but not subscripts or superscripts) indicates association into numbers greater than 9, as in 16 (= sixteen) (see p. 3, *Note*).

1.48 The *hyphen* is used to join non-consecutive locants as in 3-5 (see p. 47, Rule 6.3).

1.49 In this report, when a cipher is broken at the end of a line an em-rule is used.

1.5 *Arabic numerals are used:*

1.51 *To indicate number* (of ring atoms, etc.), (*a*) as in B6 — a 'B-type' ring of six members, and (*b*) *as locants* to describe the point of attachment of stem and substituent (see p. 3, Note).

1.52 *As subscripts*, to multiply; thus, $B6_2$ implies an aggregate of three B6 rings; $C_2/_3$ indicates three ethyl groups.

1.53 *As superscripts* placed to the left of an element symbol to indicate the mass number of isotopes, or placed to the right, to indicate abnormal valencies in elements or free radicals. Thus:

^{18}O (oxygen-18)

N^2 (bivalent nitrogen)

C^3 (methyl radical)

SECTION 2

Acyclic Hydrocarbons

Rule 2.1 *Unbranched acyclic saturated hydrocarbons* are delineated by the symbol C followed by a subscript numeral to indicate the number of carbon atoms in the chain. The subscript '1' is omitted where it would occur alone.

Examples:

Compound		Cipher	Compound		Cipher
CH_4	Methane	C	C_8H_{18}	Octane	C_8
C_2H_6	Ethane	C_2	$C_{10}H_{22}$	Decane	C_{10}
C_3H_8	Propane	C_3	$C_{20}H_{42}$	Eicosane	C_{20}
C_4H_{10}	Butane	C_4	$C_{100}H_{202}$	Hectane	C_{100}

Rule 2.2 *Hydrogen atoms* are not cited in ciphering acyclic hydrocarbons. When a structural formula is reconstructed from a cipher, the carbon structure is drawn first and hydrogen atoms are then added to complete the valencies as set out in Table 3 (see p. 82).

Rule 2.3 *Numbering unbranched saturated hydrocarbons.* Unbranched chains are numbered from one end carbon atom to the other.

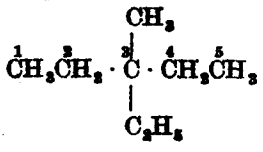
Example:

$$\overset{1}{C}H_3\overset{2}{C}H_2\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_2\overset{6}{C}H_3$$

(1)

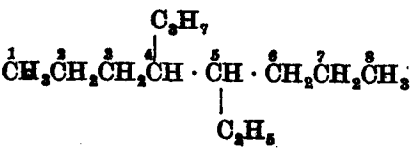
Rule 2.41 *Branched acyclic saturated hydrocarbons* are ciphered by citing the longest carbon chain followed by the branches in descending order of seniority (see p. 6; Rules 2.61–5). The position of a branch is indicated by a number placed immediately after the citation of the branch.

Examples:



(2)

$C_5C_2{}_3C_3$



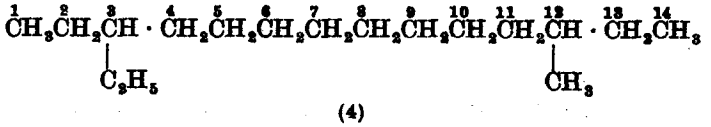
(3)

$C_8C_2{}_4C_2{}_5$

Note In example (3) the '4' following C_2 indicates that the C_2 is joined to the longest chain at position '4' of the latter. The numbers which indicate

position are called 'locants'. Locants higher than nine are underlined; subscripts are never underlined (see Rule 1.47).

Example:

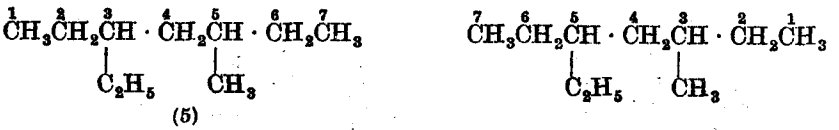


(4)

$C_{14}C_2 3C\underline{12}$

Rule 2.42 *Locants of attachment of branches.* The direction of numbering the longest chain is chosen so that the locant of the senior branch (Rules 2.61–5) affected by the choice is as low as possible.

Examples:

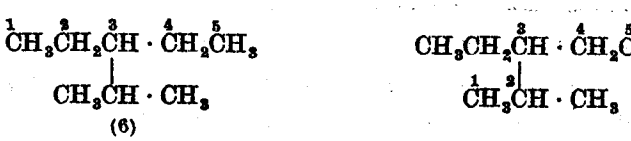


(5)

$C_7C_2 3C5$ *not* $C_7C_2 5C3$

Rule 2.43 If the *main (longest) chain can be selected in two or more ways*, it is chosen so that the groups attached to it are of maximum seniority.

Example:



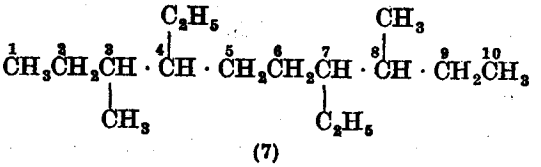
(6)

$C_5(2C_3)3$ *not* $C_5C_2 3C2$

(See also p. 5, Rule 2.51).

Rule 2.44 When *several identical groups* are attached to the longest chain, the locants of such groups are placed in ascending numerical order after the single citation of the branch.

Example:



(7)

$C_{10}C_2 47C38$

Rule 2.45 An *arithmetical series of locants*, of five or more, is replaced by the abbreviated form a[n]b, where a and b are the *lowest* and *highest* terms of the series respectively, and n is the *common difference*.

Examples:

1[1]5 for 12345 3[3]$\underline{27}$ for 369$\underline{12}$ $\underline{15}$ $\underline{18}$ $\underline{21}$ $\underline{24}$ $\underline{27}$

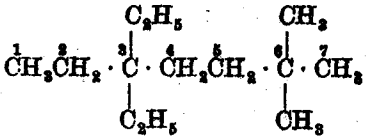
(8)

Note 1 If all the numbers in the series contain two digits or more, this rule is extended to a series of four such numbers. Thus, 22232425 is written as 22[1]25.

Note 2 This rule is general for all locant series.

Rule 2.46 The presence of *two identical groups on the same carbon atom* of a main chain is signified by a subscript numeral after the locant.

Example:



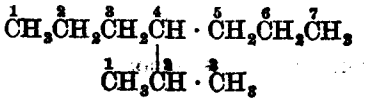
(9)

$C_7C_2{}_3{}_2C6_2$

Note This rule is general (see p. 15).

Rule 2.51 *A branch is cited in parentheses* except when it is an unsubstituted, unbranched chain attached by one of its end carbon atoms. The locant, indicating where in the main chain a branch is attached, is placed after the parentheses. The locant indicating where in a branch it is attached to the main chain is placed inside and at the beginning of the parenthetical portion.

Example:

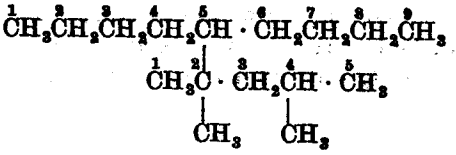


(10)

$C_7(2C_3)4$

Rule 2.52 A side chain of a branched saturated hydrocarbon is numbered independently of the main chain (that is, as if the main chain did not exist). If the side chain is unbranched (and attached by one of its terminal carbon atoms to the main chain) it is numbered outwards from the main chain. If the side chain is branched, the longest chain in the side chain which is directly attached to the main chain is numbered first, and its branches are included within the parentheses. Hence, branching in a side chain establishes in it a fixed enumeration.

Example:

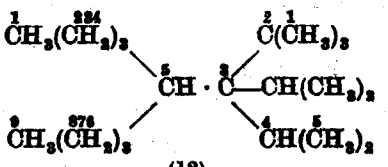


(11)

$C_9(2C_5C24)5$

Rule 2.53 If the notation of a complex structure according to Rules 2.1–2.52 leads to an expression with secondary parentheses, as in —(—(—)—), such a compound is ciphered by assembly notation (see Section 4, p. 23).

Example:



(12)

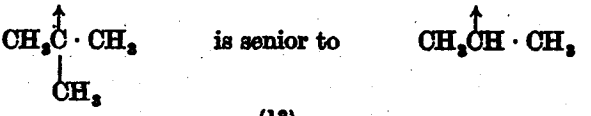
$C_9(3C_5(2C_2)3C2_24)5$

This cipher exhibits secondary parentheses and is, therefore, incorrect; the correct cipher (by assembly notation) is $C_9{:}5/3C_5(2C_2)3C2_24$; the method of arriving at this cipher is explained in Section 4.

2.6 ***Rules for determining seniority in acyclic hydrocarbon branches.***

Rule 2.61 The branch with *most carbon atoms* is senior.

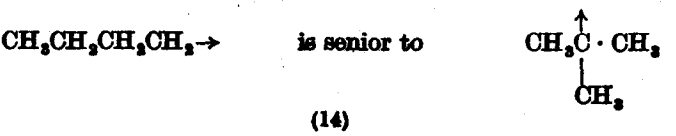
Example:



(13)

Rule 2.62 If the numbers of carbon atoms are equal the branch with *the longest chain* is senior.

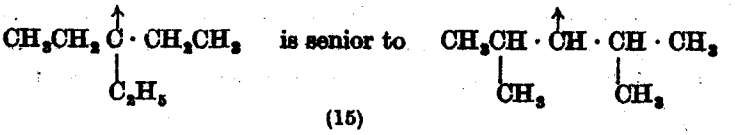
Example:



(14)

Rule 2.63 Branches having the *same number of carbon atoms and equal longest chains* are compared as to the length of their subsidiary chains; the one with the longest subsidiary chain is senior.

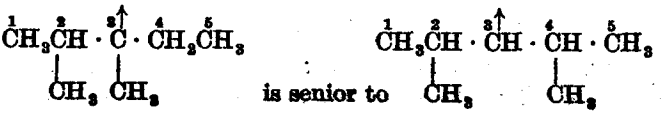
Example:



(15)

Rule 2.64 *Branches equal in number of carbon atoms and in the lengths of all chains* including the sub-branches are compared as to locants; the branch in which a lower locant first occurs in the cipher is senior. This consideration ignores the locant indicating at what atom in the branch it is attached to the main chain.

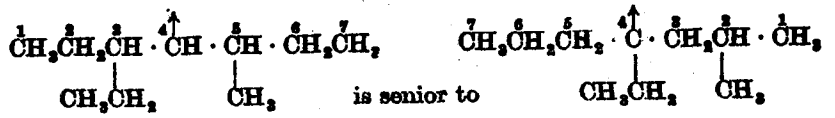
Example:



(16)

$\ldots C_5\dot{C}23$ $\qquad\qquad$ $\ldots C_5C24$

and



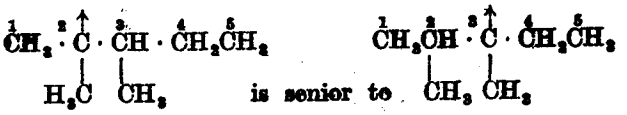
is senior to

(17)

. . . C_7C_23C5 . . . C_7C_24C2

Rule 2.65 If *groups are identical in all other respects*, that with the lowest locant of attachment to the main stem is senior.

Examples:

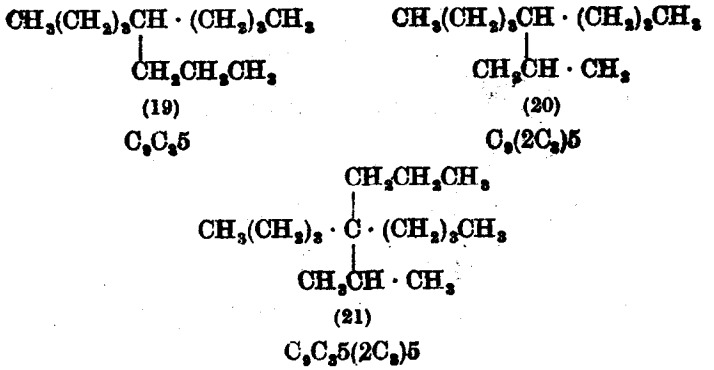


is senior to

(18)

. . . $(2C_5C23)$ . . . $(3C_5C23)$

Note In the two structures (19) and (20) the propyl and isopropyl groups occur; the former is senior to the latter, as may be seen in example (21) where both groups are present together.



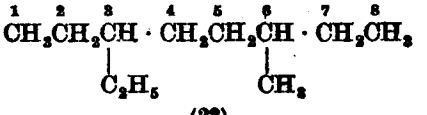
(19) C_9C_35

(20) $C_9(2C_3)5$

(21)

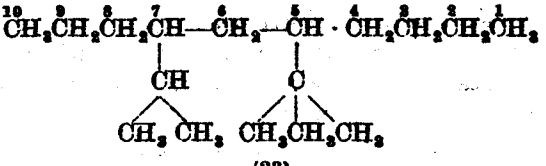
$C_9C_35(2C_3)5$

2.66 Some examples of the application of the seniority rules 2.61–2.65:



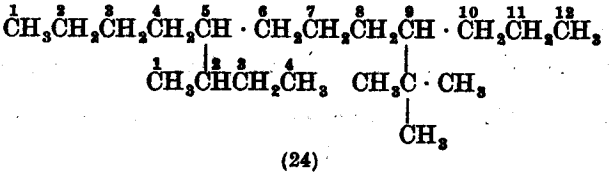
(22)

C_8C_23C6 *not* C_8C_26C3 (Rule 2.61)



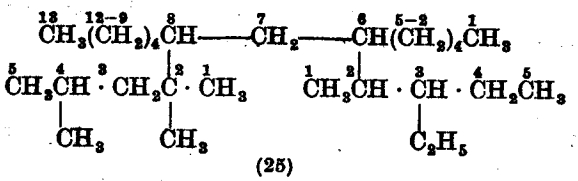
(23)

$C_{10}(2C_2C2)5(2C_3)7$ *not* $C_{10}(2C_2C2)6(2C_3)4$ (Rule 2.61)



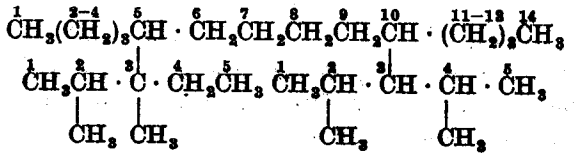
(24)

$C_{12}(2C_4)5(2C_3C2)9$ (Rule 2.62)



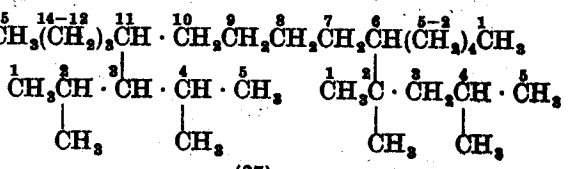
(25)

$C_{18}(2C_5C_2)3)6(2C_5C24)8$ (Rule 2.63)



(26)

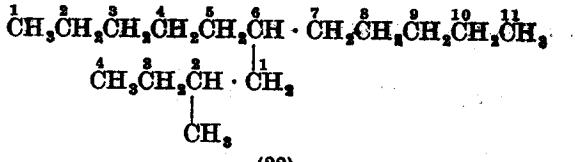
$C_{14}(3C_5C23)5(3C_5C24)\underline{10}$ (Rule 2.64)



(27)

$C_{15}(2C_3C24)6(3C_5C24)\underline{11}$ (Rule 2.65)

Rule 2.67 A locant '1' coming just inside an opening parenthesis is omitted. *Example:*



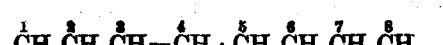
(28)

$C_{11}(C_4C2)6$

2.7 *Unsaturation in acyclic hydrocarbons.*

Rule 2.71 ***Unsaturation in acyclic hydrocarbons*** **is denoted by E for a double bond and Y for a triple bond, followed by the locant which must be as low as possible after the locants of any branches have been established. When a double bond unites one carbon atom numbered (n) to another numbered (n + 1) the locant 'n' is used to define its position. Hence if, in a chain, carbon atoms at positions '3' and '4' are joined by a double bond this is signified by 'E3'.**

Example:

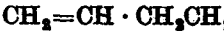


(29)

C_8E3

Rule 2.72 The locant '1' where it might occur at the end of a cipher or the beginning or end of a parenthesis is omitted. This rule is general.

Examples:

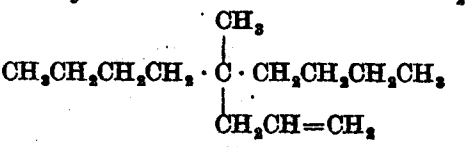


(30)

C_5E

(31)

C_2Y

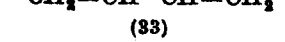


(32)

$C_9(3C_3E)5C5$

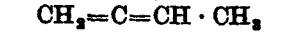
Rule 2.73 *Multiple unsaturation* is ciphered by multiple locants for E or (and) Y; if five or more units of either kind of unsaturation are present in a chain so that the locants form an arithmetical series, the locants are expressed by the method of Rule 2.45 (see example 36).

Examples:



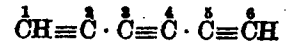
(33)

C_4E13



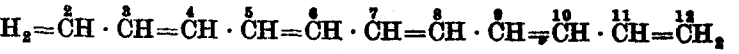
(34)

C_4E12



(35)

C_6Y135

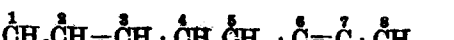


(36)

$C_{12}E1[2]11$

Rule 2.74 In ciphers of ***hydrocarbons containing both double and triple bonds*** the former are cited first and are held to be senior, as in establishing the direction of numbering a main chain.

Example:

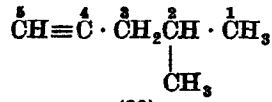


(37)

C_5E2Y6

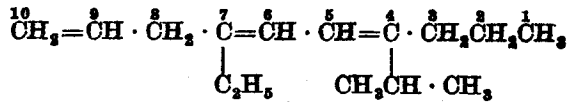
Rule 2.75 *Unsaturation in a main chain* is cited after the citation of carbon side chains.

Examples:



(38)

C_5C2Y4

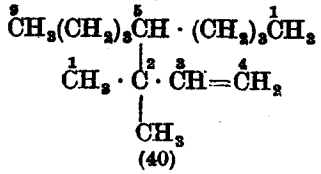


(39)

$C_{10}(2C_3)4C_2{}^7E469$

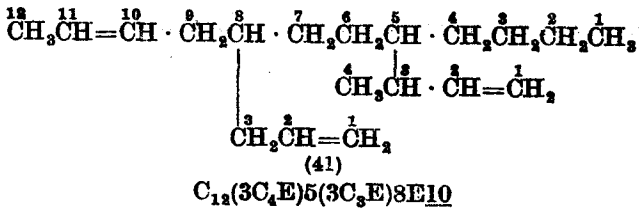
Rule 2.76 *Unsaturation in branches* is cited within the appropriate parentheses and confers a fixed enumeration on a side chain, if such has not already been established by carbon sub-branches. Unsaturation in branches is given as low locants as possible, after the locants of the carbon sub-branches have been assigned. If these rules lead to secondary parentheses assembly notation is used (see p. 23).

Examples:



(40)

$C_9(2C_4C2E3)5$

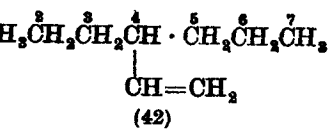


(41)

$C_{12}(3C_4E)5(3C_3E)8E\underline{10}$

Note Parentheses are omitted from the citation of unsaturated side chains whose citation does not require a locant within the parentheses. Thus C_2E and C_3E are cited without parentheses and imply the side chains $—CH=CH_2$, and $—CH=CH\cdot CH_3$ respectively, whereas $—CH_2CH=CH_2$ is ciphered as $(3C_2E)$. This rule is general for all substituted side chains.

Example:

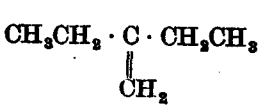


(42)

C_7C_2E4

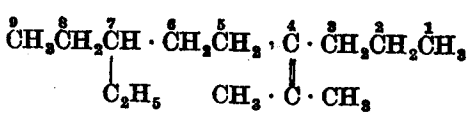
Rule 2.77 *If the double bond lies between the main chain and a branch* the symbol E is placed before the branch citation, and immediately inside the parentheses, before the locant of attachment of the branch to the chain, if parentheses are necessary.

Examples:



(43)

C_5EC3



(44)

$C_9(E2C_3)4C_2{}^7$

Rule 2.78 *Seniority and unsaturation.* Chains and branches identical under Rules 2.61–2.64 acquire seniority when unsaturated. All such chains and branches are cited in order of decreasing seniority. Seniority increases in order of increasing total number of double and triple bonds. Of two branches having the same total number of double and triple bonds, the senior is that having most double bonds. If both double and triple bonds are equally represented in both branches, that in which a lower locant first occurs is senior.

Examples: The following groups are arranged in order of increasing seniority:

(45) $CH_3CH_2\underset{|}{C}H \cdot CH_2CH_3$ ... $(3C_5)$

(46) $CH{\equiv}C \cdot \underset{|}{C}H \cdot CH_2CH_3$ ... $(3C_5Y)$

(47) $CH_2{=}CH \cdot \underset{|}{C}H \cdot CH_2CH_3$ ... $(3C_5E)$

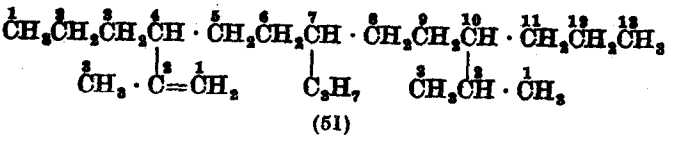
(48) $CH{\equiv}C \cdot \underset{|}{C}H \cdot C{\equiv}CH$ ... $(3C_5Y14)$

(49) $CH_2{=}CH \cdot \underset{|}{C}H \cdot C{\equiv}CH$ ... $(3C_5E1Y4)$

(50) $CH_2{=}CH \cdot \underset{|}{C}H \cdot CH{=}CH_2$ ... $(3C_5E14)$

increasing seniority ↓

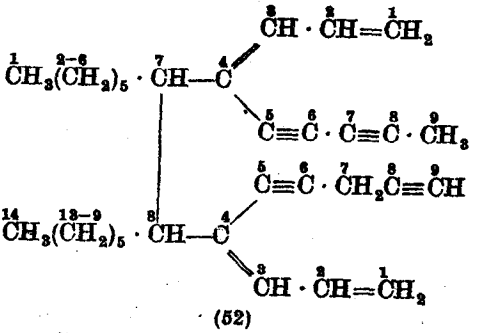
Note In ciphering example (51) it will be noted that the longest chain is C_{13} and is cited first. There are three 3-carbon side chains; of these C_3E is senior by virtue of its double bond and is cited first; at the same time it determines the direction of numbering the main chain. Of the two remaining 3-carbon side chains C_3 is senior to $(2C_3)$ since the former is attached by carbon '1' to the main chain (see Rule 2.65).



(51)

$C_{13}(2C_3E)4C_37(2C_3)\underline{10}$

Additional example:



(52)

$C_{14}(4C_3E13Y57)7(4C_3E13Y58)8$

Note The choice of the main chain of example (52) is governed by Rule 2.43, that is, so that the side chains are of maximum seniority.