mental conditions of feeding. On the basis of rotatory data it seems unlikely that 6,x-anhydro-menthyl glucoside and 6,y-anhydro-methyl glucoside are derivatives of the same anhydro-glucose. Lastly, it is pointed out on theoretical grounds that glucuronic lactone and the salts, amides, etc., of glucuronic acid may possibly occur in two isomeric forms corresponding to the alpha and beta forms of glucose and may exhibit mutarotation.

WASHINGTON, D. C.

PROPOSED INTERNATIONAL RULES FOR NUMBERING ORGANIC RING SYSTEMS

BY AUSTIN M. PATTERSON

RECEIVED NOVEMBER 7, 1924 PUBLISHED FEBRUARY 5, 1925

Preface

In 1921, the author reported to the Board of Editors of the JOURNAL OF THE AMERICAN CHEMICAL SOCIETY that data upon organic ring systems and their systematic numbering had been accumulated in connection with the indexing of *Chemical Abstracts*, and asked whether it would be advisable to publish a catalog of such systems, in the JOURNAL or elsewhere. The Board decided that it would be, but felt it extremely desirable to secure beforehand a wide agreement among chemists as to the numberings.

A joint committee of the American Chemical Society and the National Research Council, consisting of J. F. Norris, *chairman*, M. T. Bogert, J. W. Kinsman, W. A. Noyes and A. M. Patterson, was appointed to coöperate with the author. Rules for numbering ring systems were drawn up and submitted to this Committee and later to the Committee on Organic Nomenclature of the International Union of Pure and Applied Chemistry, consisting of A. F. Holleman (Netherlands), *chairman*, A. J. Greenaway (Great Britain), R. Marquis (France), E. Paternò (Italy), A. Pictet (Switzerland) and A. M. Patterson (United States). They were also shown unofficially to the late Prof. Jacobson and to Dr. Stelzner, of Germany. Several drafts were made and much improvement resulted from the criticisms.

In their present form the Rules have been approved by the International Committee for a provisional period of two years, during which they will be open for the criticism of chemists generally. At the end of that period, if no fundamental objections are found to the Rules, the expectation is that they will be finally adopted for use in the journals of the respective countries, with any further improvements or corrections that may have been suggested.

Considerable time has been given to devising a set of Rules that shall be applicable to all systems of simple or fused rings and yet be as simple and clear as possible and preserve a maximum of the numberings now in use. The present article embodies the best results achieved to date. The ring systems described in Beilstein's "Handbuch," Richter's "Lexikon," Stelzner's "Literatur-Register" and the 18 volumes of *Chemical Abstracts* have been carefully checked and the numberings compared.

If and when the Rules are put into effect in the journals, they should be as free from causes for objection as they can be made. It is urged that anyone having criticisms to make send them promptly to the author, to Prof. Norris, or to his own representative on the International Committee. The question whether hydrogen atoms should be favored for low numbers in all classes is an important one, and the recommendations of organic chemists are especially desired on this point (see "Position of Double Bonds," under *Comments*).

Publication of the catalog of ring systems will be deferred, pending the final adoption of the Rules.

The author wishes to acknowledge his indebtedness to the members of the Committees and especially to Prof. W. A. Noyes, who has taken a most active interest in the progress of the Rules and served as the author's substitute at meetings of the International Committee.

Rules and Notes

Note 1. The word "system" is used to mean a single ring or a combination of rings united one to another by atoms common to both ("fused" systems). Rings united only by a valence bond as in biphenyl ($C_6H_5—C_6H_5$), or by an intermediate atom or chain as in diphenylmethane ($C_6H_5CH_2C_6H_5$), are not considered as parts of the same ring system for the purposes of these Rules.

Note 2. Derivatives. Although the following Rules determine the numbering of parent systems *in all degrees of hydrogenation,* it is not the intention to fix the position of hydrogen atoms in all their derivatives. All that is required of derivatives is *that their numbering conform to that of the lowest stage of hydrogenation of the parent system in Classes A II, B and C II, and to that of the saturated form in A I, C I, C III and D I.* For example, the Rules assign the positions 1–4 to the CH_2 groups in "tetralin," which numbering corresponds to the name 1,2,3,4-tetrahydronaphthalene. But this does not prevent the naming and numbering of an hydroxyl derivative of it as 5,6,7,8-tetrahydro-2-naphthol; the numbering of the latter is based on that of naphthalene, the least saturated form of the parent system. (Decision between two or more alternative numberings of derivatives in such cases is a separate matter lying outside the scope of the Rules; for one system of making such decisions see *J. Am. Chem. Soc.*, **39,** 1628 ff.) Conversion of a derivative to the lowest stage of hydrogenation of the parent system may involve (1) replacement of substituting atoms or groups by hydrogen, (2) removal of hydrogen atoms in pairs, (3) removal of O_2, CH_3Cl, etc., from ring atoms if the latter can thereby pass to a well recognized lower state of valence, (4) introduction of quinoid structure, or rarely (5) conversion of trivalent into pentavalent nitrogen. It should *not* involve the introduction of triple bonds, two double bonds attached to the same carbon atom, or new bridging bonds. In some cases there will be two or more isomeric least saturated forms which may equally well be regarded as the parent of the derivative.

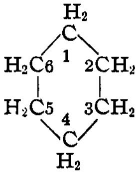
Note 3. Lowest Numbers. The expression "lowest numbers," as used in connection with the Rules, signifies the numbers yielding the smallest sum or, if the sums are equally small, those that include the lowest individual number or numbers. Thus, 1,3,5 is lower than 2,4,6; 1,4,5 is lower than 2,3,5; 1,2,5 is lower than 1,3,4; 1,1,3,4 is lower than 1,2,2,4.

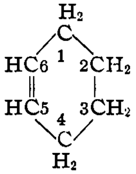
A. The system consists of a single ring.

I. The ring is carbocyclic.

Rule 1. Number around the ring in such a manner as to give to hydrogen atoms the lowest numbers possible.

Examples:


I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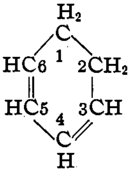
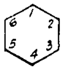

III


(Benzene)
IV

Note 4. Fixed orientations are an aid to memory and should not be neglected. Single rings should be oriented with Position 1 at the top and with the numbers proceeding clockwise around the ring.

II. The ring is heterocyclic.

Rule 2. Choose as starting point a hetero atom of as high a group in the periodic table of the elements, and as low an atomic number in that group, as possible.

Note 5. The following order as determined by the above rule, includes the commonly occurring hetero atoms: O, S, Se, Te, N, P, As, Sb, Si, Sn, Pb, Hg.

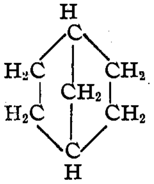
Rule 3. With an atom of the preferred kind as 1, number around the ring in the way that gives to hetero atoms the lowest numbers possible.

Rule 4. *Of two or more numberings conforming to Rules 2 and 3, choose the one that assigns low numbers most nearly in the order of precedence established in Rule 2.*

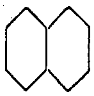
Rule 5. *Of two or more numberings conforming to Rules 2–4, choose the one that gives to hydrogen atoms the lowest numbers possible.*

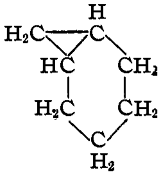
B. The system contains at least two rings of five or more members, but no atomic bridges, crossed valence bridges or free spiro unions.

Note 6. An "atomic bridge" is one that contains atoms (*e. g.*, the bridge in norcamphane, V) as contrasted with a "valence bridge" (*e. g.*, that in naphthalene, VI, or in norcarane, VII). The "peri" forms frequently encountered among aromatic compounds are included in Class B and are *not* treated as having an atomic bridge, although strictly speaking they do contain one. For example, acenaphthylene, VIII, is a "peri" form and the black dot represents a carbon atom. Such forms may be regarded as resulting from three ordinary or "ortho" fusions: A with B, B with C, and A with C.

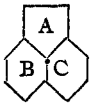


V


VI



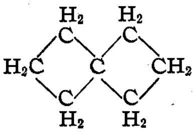
VII



VIII

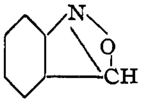
Note 7. "Crossed valence bridges" are valence bridges that are represented by the plane formula as crossing each other, as shown in Example XLVIII.

Note 8. A "spiro union" is one formed by a single atom which is the only common member of two rings. A "free spiro union" is one constituting the *only* union, direct or indirect, between two rings, as in IX. Systems in which the rings are united in some other way (that is, by intermediate rings) as well as by the spiro union are not necessarily excluded from Class B.

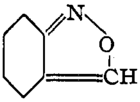


IX

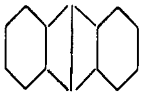
Note 9. In determining whether or not a system contains at least two rings of five or more members, one counts as component rings *only* *the smallest number of smallest rings that together will account for all the atoms and valences.* Thus, in Example VII it is possible to see a 3-ring, a 6-ring and a 7-ring, yet it is called a "3,6" system because the 3-ring and the 6-ring together account for all the atoms and valences and the 7-ring is merely the circumference of the fused 3- and 6-rings; the system does not belong in Class B. Valence bridges which are sometimes used to account for the chemical peculiarities of a compound but which are not absolutely indispensable in representing the formula are not considered in these Rules. The bridge sometimes shown between N and CH in one formula for anthranil (X) is a case in point, for a formula may be written for it without this bridge, as in XI: it is therefore classed as a 5,6 system and placed in Class B. The middle bridge sometimes shown in the formula for anthracene is another example. Anthracene is treated not as a 4-ring system (XII) but as a 3-ring system (XIII).



X



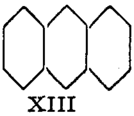
XI



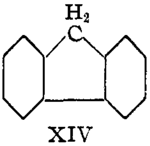
XII

Rule 6. Orient the formula so that the greatest possible number of rings will be in a horizontal row.

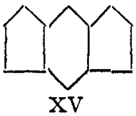
Note 10. Triangles in such a row should have one side vertical, other rings two sides vertical (this requires a deformation of the polygons with an odd number of sides, thus:  or ). Accordingly, hexagons should have angles, not sides, at top and bottom. Anthracene (XIII) constitutes a horizontal row of three, so do fluorene (XIV) and *s*-indacene (XV); but phenanthrene (XVI) does not.



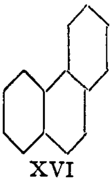
XIII



XIV



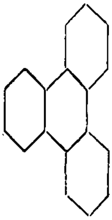
XV

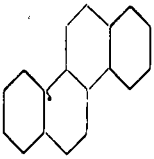


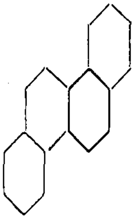
XVI

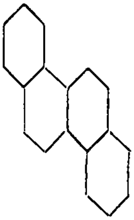
Rule 7. Of orientations conforming to Rule 6, choose the one that places as many as possible of the remaining rings above and to the right.

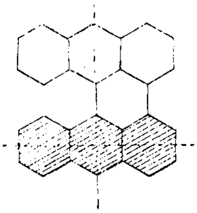
Note 11. Only the *number* of rings and not their size or distance from the center, is taken into account. When the correct orientation is not immediately apparent, bisect the "horizontal row" by a horizontal axis and a vertical axis (as in XXI) and count the rings and fractions of rings in the four quadrants. If there is more than one combination of rings that could serve as the "horizontal row," apply the bisection in the other cases also (as in XXII). Choose the orientation that has as many as possible of the "remaining rings" in the upper right quadrant; if two or more orientations meet this requirement, choose the one of them that has as few rings as possible in the lower left quadrant. In the examples, phenanthrene (XVI) is shown correctly oriented with its single "remaining ring" turned upward toward the right; triphenylene (XVII) has one in the upper right quadrant and one in the lower right; Examples XVIII–XX show right and wrong orientations of chrysene; and XXI and XXII show right and wrong orientations in a case that might not be immediately apparent.

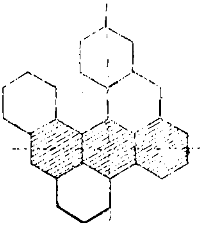

XVII


XVIII (right)


XIX (wrong)

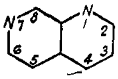

XX (wrong)


XXI (right)

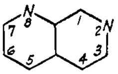

XXII (wrong)

Rule 8. Of orientations conforming to Rules 6 and 7, choose the one that gives the lowest numbers to hetero atoms when the formula is numbered as directed below (Rule 12).

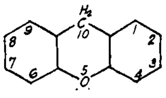
Examples:



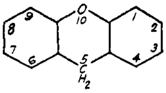
XXIII (right)



XXIV (wrong)



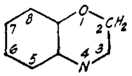
XXV (right)



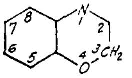
XXVI (wrong)

Rule 9. Of orientations conforming to Rules 6–8, choose the one that assigns low numbers to hetero atoms most nearly in the order of precedence given in Rule 2.

Examples:



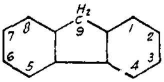
XXVII (right)



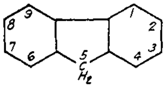
XXVIII (wrong)

Rule 10. *Of orientations conforming to Rules 6–9, choose the one in which unnumbered carbon atoms follow the lowest numbers possible.*

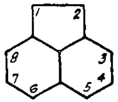
Examples: In XXIX the unnumbered carbon atoms follow the numbers 4,4,8,9; these are lower than the 4,5,9,9 of XXX. Similarly, the numbers 2,5,8 of XXXI are lower than the 3,5,8 of XXXII.



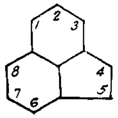
XXIX (right)



XXX (wrong)



XXXI (right)

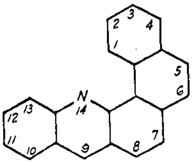


XXXII (wrong)

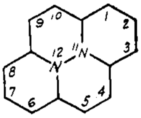
Rule 11. *Of orientations conforming to Rules 6–10, choose the one that gives to hydrogen atoms the lowest numbers possible.*

Rule 12. *Number the oriented formula by beginning with the first free angle of the upper right ring and proceeding clockwise around the entire formula to the beginning, numbering all carbon atoms that are not common to two or more rings, and all hetero atoms. Number interior hetero atoms last of all, following the shortest path from the highest previous number.*

Examples: (See also XXIII–XXXII)



XXXIII



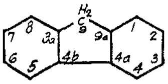
XXXIV

Note 12. The "first free angle" is the first angle, not also part of another ring, from which one may proceed clockwise around the ring.

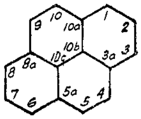
Note 13. The "upper right ring" is the highest ring in the formula or, if two or more are equally high, then the ring farthest to the right in the highest row.

Note 14. Ordinarily, no numbers are needed for carbon atoms that are common to two or more rings. When such a need does arise, it is recommended that they be numbered by adding *a* (or *b*, *c*, etc., in case of a succession of them) to the number of the position just preceding in the clockwise order; interior carbon atoms are considered to follow the highest number.

Examples:



XXXV



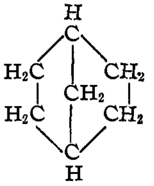
XXXVI

Note 15. Formulas should always be represented in their correct orientation because the maintaining of a fixed position is a valuable aid to memory. If one has a mental picture of the oriented formula, he can readily renumber it at any time by Rule 12.

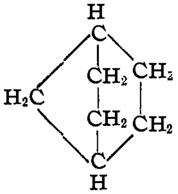
C. The system does not belong to Classes A and B, and does not contain free spiro unions.

I. The system consists of two rings only, separated by either an atomic bridge or a valence bridge.

Note 16. Formulas of systems belonging to Class C I must be drawn so that the bridge contains as few members as possible. Examples:



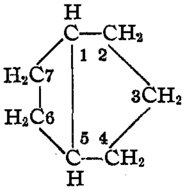
XXXVII (right)



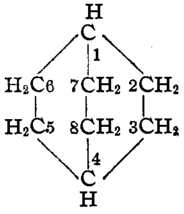
XXXVIII (wrong)

Rule 13. *Starting with one end of the bridge as 1, number around the longer way to the other end of the bridge, then on around the shorter way to the beginning and finally, by the shortest path, along the bridge itself if the bridge is atomic. If there are two or more possibilities for the shortest path, choose the shortest path from the highest previous number that will give a decision. Number all ring members.*

Examples:



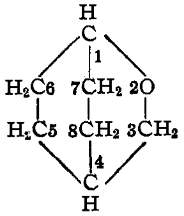
XXXIX



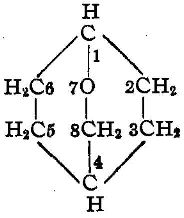
XL

Rule 14. *Of numberings conforming to the above rule, choose the one that gives the lowest numbers to hetero atoms.*

Examples:



XLI (right)



XLII (wrong)

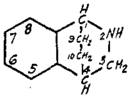
Rule 15. *Of numberings conforming to the above rules, choose the one that assigns low numbers to hetero atoms most nearly in the order of precedence given in Rule 2.*

Rule 16. *Of numberings conforming to the above rules, choose the one that gives to hydrogen atoms the lowest numbers possible.*

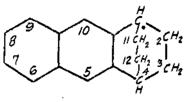
II. The system contains one or more atomic bridges the removal of which would throw the system into Class B.

Rule 17. *Disregarding the atomic bridges and converting the resulting form to the lowest stage of hydrogenation, number by Rules 6–12; then number the bridge members, following the shortest path as in Rule 13.*

Examples:



XLIII



XLIV

Note 17. The atomic bridges in Class C II must contain as few members as possible and, the number of members having been determined, as few hetero atoms as possible. After the outside numbers have been determined by Rules 6–12, the formula must be so oriented that the ends of the atomic bridges receive the lowest numbers possible. For example, Formula XLIII is so drawn that the NH group is part of an outside ring and not of the bridge, so that it may receive as low a number as possible. In XLIV the bridge is shown between Positions 1 and 4, not between 6 and 9.

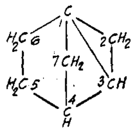
For conversion to the lowest stage of hydrogenation, see Note 2.

III. The system does not belong under I or II.

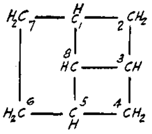
Note 18. The systems of Class C III contain two or more bridges, either atomic or valence. Special care must be taken to draw the formula so that the bridges shall be as simple and of as few members as possible.

A branched bridge is regarded as consisting of a main bridge and one or more branch bridges. A branched bridge should be preferred to crossed bridges even though it contains more members (see XLVII and XLVIII), but in no case should the chain of bridge members between the two bridge ends be greater than either of the outside chains between the same points. In difficult cases it may be advisable to construct a spatial model so as to decide upon the most natural plane formula.

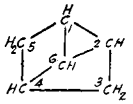
Examples:



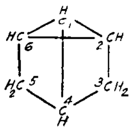
XLV



XLVI



XLVII (right)



XLVIII (wrong)

Rule 18. *Select as the chief bridge (one end of which becomes Position 1) the one having the most members or, if two have an equally large number of members, the one that divides the outside ring more symmetrically; then number as in Rule 13; then number any remaining bridge members by the shortest path.*

Examples: See XLV, XLVI, XLVII.

Note 19. If a branched bridge is present, part of it may constitute the chief bridge; for example, in XLVI, 1–8–5 is the chief bridge and 3–8 is the other bridge.

Rule 19. *Of two or more numberings conforming to Rule 18, choose the one that gives the lowest numbers to the ends of the other bridges.*

Example: See XLV.

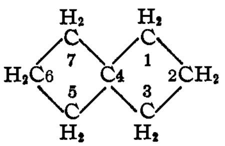
Rule 20. *If two or more numberings are possible in conformity with Rules 18 and 19, apply Rules 14–16.*

D. The system contains one or more free spiro unions.

I. The system contains spiro unions only.

Rule 21. *Beginning with a ring member next to the spiro atom in the right end ring, number clockwise around the end ring and on around the entire formula. Number all ring members.*

Example:

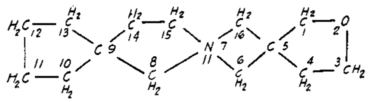


XLIX

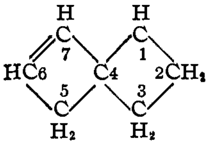
Rule 22. *Of two or more numberings conforming to Rule 21, choose the one that gives the lowest numbers to spiro atoms.*

Rule 23. *If there are two or more numberings conforming to Rules 21 and 22, apply Rules 14–16.*

Examples:



L

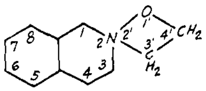


LI

II. The system contains other ring unions in addition to spiro unions.

Rule 24. *(Provisional.) Treat separately each complex united by a free spiro union to another complex, giving to each the numbering it would have separately under the foregoing rules, but distinguishing the numberings from one another (as by primes). Give to the spiro atoms as low numbers in each complex as is consistent with the numbering of that complex.*

Example:



LII

Comments

Position of Double Bonds.—Opinions of chemists are divided as to whether saturated or unsaturated linkages should be given the preference in assigning low numbers. Usage in the past has apparently favored one practise for certain classes of rings and the reverse for certain others. There seems to be a feeling that practise should be uniform and the Rules as now formulated favor saturated linkages for low numbers in all classes. This number accords with such names as 1,2-dihydrobenzene, 1,2,3,4-tetrahydronaphthalene and 1,2-pyran, but not with such as 1-cyclopentene and Δ^2-pyrroline.

To favor *un*saturated linkages for low numbers in all classes would, in the opinion of the author, be less satisfactory. The fact is, that in certain classes compounds are usually named on the basis of parent forms low in hydrogen (as with furan, anthracene) while in others the compounds are usually named on the basis of saturated parent forms. Hence in the former classes the names tend to give low numbers to hydrogen atoms (as with 1,2-pyran, 1,2-dihydro-anthracene) while in the latter classes the names tend to give low numbers to double bonds (as with 1-cyclopentene, 1-spiroheptene). The two systems overlap in such cases as 1,2,3,4-tetrahydrobenzene (1-cyclohexene). Perhaps the Rules should recognize and embody this contrast. However, if chemists are willing to use such names as 4-cyclopentene and 6-spiroheptene, or to adopt some other way of expressing the high numbers of the double bonds in these compounds, the present Rules ought to work satisfactorily. They at least have the merit of being simpler thus, but an ideal solution has not yet been attained.

Numbering of Classes A and B.—The principles employed in numbering systems of these classes are in general those used in M. M. Richter's "Lexikon der Kohlenstoffverbindungen" (see pages 14–26 of the introduction to the third edition); but inconsistencies have been eliminated and all hetero atoms are required to be numbered. Of the 311 numbered formulas of Classes A and B given by Richter, 73 per cent. conform to the Rules; if Richter had numbered all hetero atoms, 88 per cent. would have conformed.

If the Rules are applied without exception, the commonly accepted numbering of a few well-known parent forms, including anthracene, phenanthrene, acridine, xanthene and purine will have to be changed. Serious consideration has been given to introducing special rules in order to preserve some of these accepted numberings, and also to making outright exceptions of them. The overwhelming sentiment of organic chemists who have been consulted has, however, been in favor of keeping the Rules as simple as possible and making no exceptions. An elaborate attempt has been made by Stelzner and Kuh (see the 99-page article in the introduction to Vol. III of Stelzner's "Literatur-Register") to extend the principle of the commonly accepted numbering of anthracene and phenanthrene to other polycyclic systems. It leads to hopeless complications.

Definition of Class B.—This class includes the large majority of all known organic ring systems, and most of the compounds represented by them are of the aromatic type. The definition is so drawn as to exclude such systems as norcarane, bicyclo[3,1,0]hexane, etc., which are customarily numbered as systems of Class C. Any distinction between Classes B and C must be more or less arbitrary, but the line drawn in the Rules conforms fairly closely to actual usage. It would be more consistent to number the systems of Classes B and C alike and to include all ring members in the numbering, but this would run the numbers up very high in polycyclic aromatic compounds, and for the most part these additional numbers would not be used.

Numbering of Class C.—The method of numbering the bridged systems of Class C follows that of von Baeyer [*Ber.*, **33**, 3771–5 (1900)] but extends it to cover many possibilities which von Baeyer did not attempt to consider.

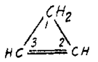
Class C II includes certain bridged systems (about forty are actually known) which are most conveniently numbered by treating them as Class B forms to which bridges have been attached.

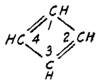
Numbering of Complex Spiro Systems.—Rule 24 has been marked "provisional" because at some later time it may be thought desirable to give directions for numbering these systems "straight around" like the preceding classes. No simple and certain way of doing this has as yet been worked out.

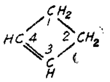
Additional Examples

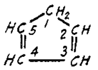
The following additional examples have been appended at the request of the International Committee for the purpose of showing more clearly the application of the Rules. From the many hundreds of known ring systems these have been selected for variety of structure and also to illustrate any possibly undesirable effect of the Rules in certain instances (see, for example, Nos. 121, 130, 131, 133, 137, 140, 148). In Classes C II and C III the chief bridge is denoted by a heavy line. "B_3" refers to Beilstein, 3rd edition; "C. A." to *Chemical Abstracts;* and "Richter" to M. M. Richter's "Lexikon" ("Ringsysteme" in Vol. I).

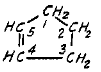
Class A I

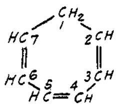

1. Cyclopropene


2. Cyclobutodiene

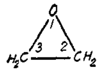

3. Cyclobutene

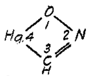

4. Cyclopentadiene

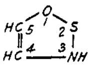

5. Cyclopentene

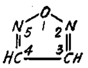

6. Cycloheptatriene (Tropilidene)

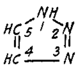
Class A II

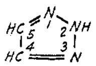

7. Ethylene oxide

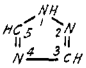

8. C. A. 18, 377

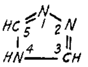

9. Isothioxazole

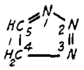

10. Furazan

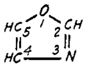

11. 1,2,3-Triazole

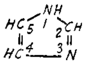

12. 2,1,3-Triazole

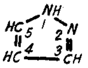

13. 1,2,4-Triazole

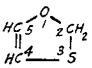

14. 4,1,2-Triazole

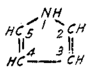

15. 1,2,3-Isotriazole

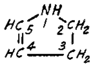

16. Oxazole

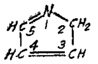

17. Imidazole (Glyoxaline)

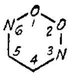

18. Pyrazole

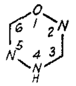

19. 1,3-Thioxole

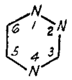

20. Pyrrole

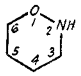

21. 1,2-Dihydropyrrole (Δ4-Pyrroline)


22. Isopyrrole

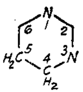

23. 1,2,3,6-Dioxdiozine


24. 1,4,2,5-Oxtriazine

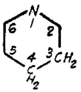

25. as-Triazine

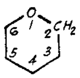

26. o-Isoxazine

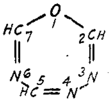

27. Pyrimidine


28. 4,5-Dihydropyrimidine

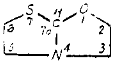

29. Pyridine

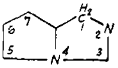

30. 3,4-Dihydropyridine

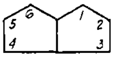

31. 1,2-Pyran

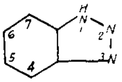

32. C. A. 16, 2334

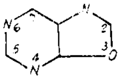
Class B

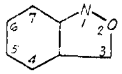

33. C A 17, 1235

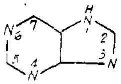

34. B_3 IV, 39

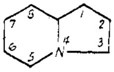

35. C A. 7, 3131 (Bicyclo[3,3,0]octatetrene)

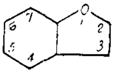

36. 1,2,3-Benzotriazole

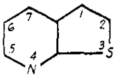

37 C A 8, 1960

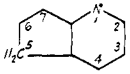

38. Anthranil

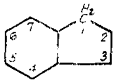

39 Purine

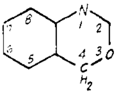

40 Pyrrocoline

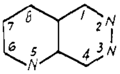

41. Benzofuran (Coumarone)

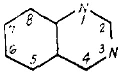

42 C A 7,1482

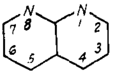

43. B_3 IV (589)

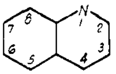

44. Indene

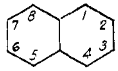

45 B_3 II, 786

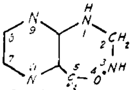

46 Richter 193

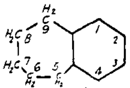

47 Quinazoline

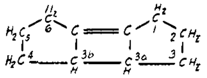

48 Naphthyridine

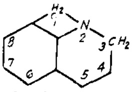

49. Quinoline

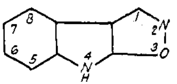

50 Naphthalene

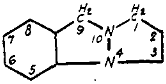

51. B_3 IV, 946

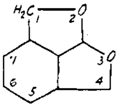

52 B, III (132)

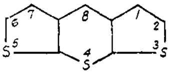

53 B_3 III (134)

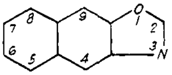

54 B_3 IV, 1220

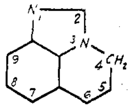

55. C A. 17, 2424

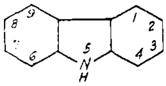

56. C A. 4, 2141

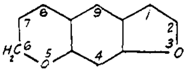

57, B_3 II (1130)

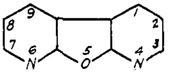

58. C.A 4, 2475

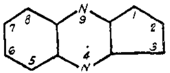

59. ββ-Napthoxazole

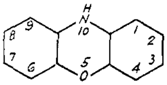

60. Quinimidazole

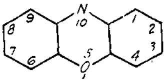

61. Carbazole

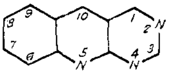

62 C A 5, 3324

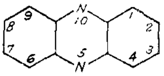

63. B_3 I (790)

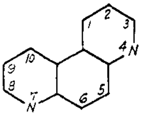

64. C A 4, 3079

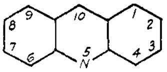

65. Phenoxazine

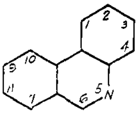

66. Phenazoxonium

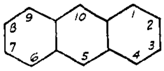

67 B_3 IV (833)

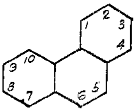

68. Phenazine

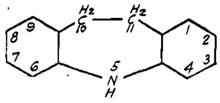

69. B_3 IV, 999

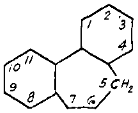

70 Acridine

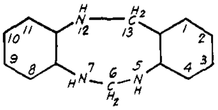

71. Phenanthridine

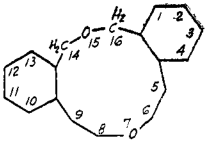

72. Anthracene

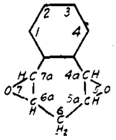

73. Phenanthrene


74. B_3 IV (237)

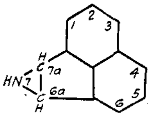

75. C A 7, 991


76. B_3 IV, 562

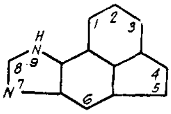

77. B_3 II, 1641



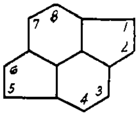
78. C.A 16, 1233



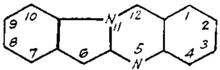
79. B_3 IV (233)



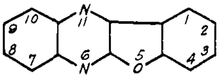
80. C.A. 6, 96



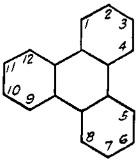
81. Pyracene



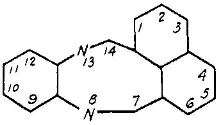
82. C.A. 16, 3654



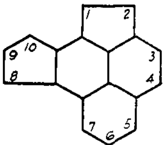
83. C.A. 16, 2688



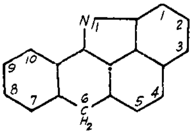
84. Triphenylene



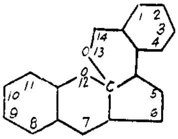
85. B_3 IV (727)



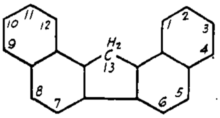
86. C.A. 15, 1702



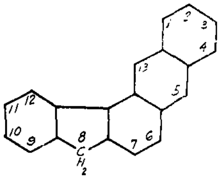
87. C.A. 5, 3813



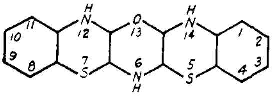
88. C.A. 7, 2383



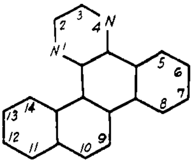
89. C.A. 3, 2558



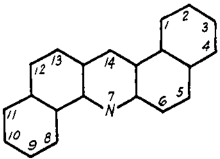
90. C.A. 8, 1586



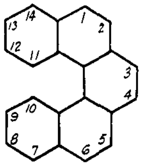
91. C.A. 10, 1535 (II)



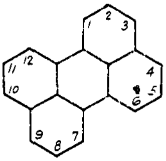
92. B_3 IV, 1087



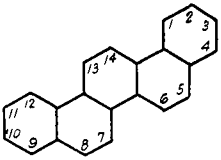
93. B_3 IV (292)



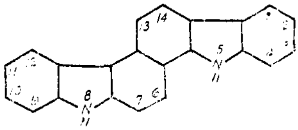
94. C.A. 13, 433



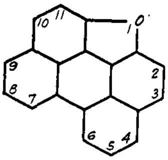
95. Perylene



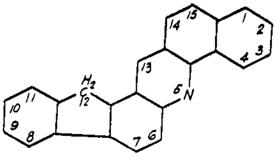
96. Picene



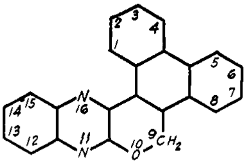
97. C.A. 16, 1955 (II)



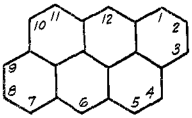
98. C.A. 7, 2947^8



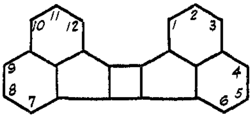
99. Richter 366



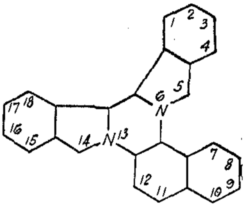
100. C.A. 7, 3477



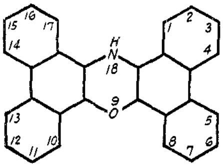
101. C.A. 8, 2877



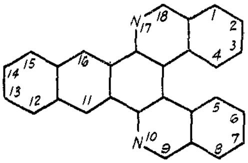
102. Heptacyclene



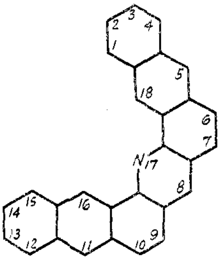
103. C.A 13, 1838



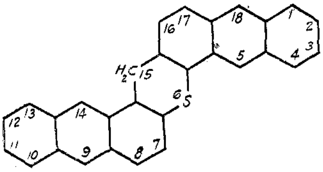
104 B_3 IV (295)



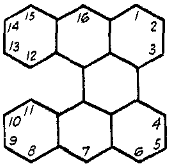
105. C.A. 18, 2169 (II)



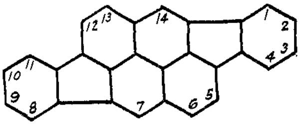
106. C.A. 6, 2932



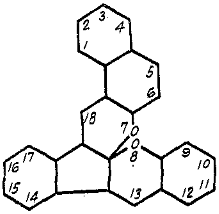
107. C.A. 9, 1759



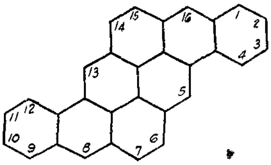
108. C.A. 2, 1633



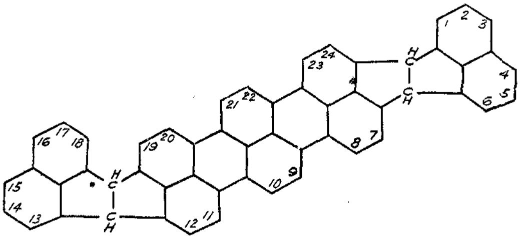
109. Marlene



110. C.A. 7, 2383

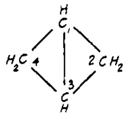


111. Pyranthrene

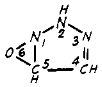


112. Leucacene (C.A. 15, 1311)

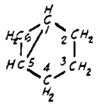
Class C I



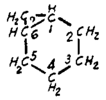
113. Bicyclo[1,1,0]butane



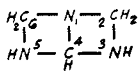
114. B_3 IV (511)



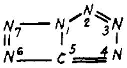
115. Bicyclo[3,1,0]hexane



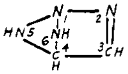
116. Bicyclo[4,1,0]heptane (Norcarane)



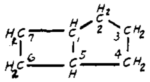
117. B_3 I, 932



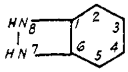
118. Richter 120



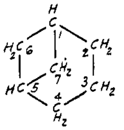
119. C.A. 17, 1641



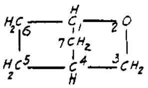
120. Bicyclo[3,2,0]heptane



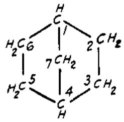
121. B_3 IV, 1245



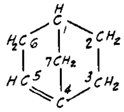
122. Bicyclo[3,1,1]heptane (Norpinane)



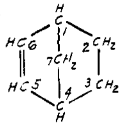
123. B_3 IV, 715



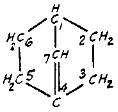
124. Bicyclo[2,2,1]heptane (Norcamphane)



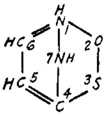
125. Bicyclo[2,2,1]hept-4-ene



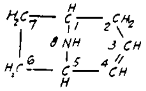
126. Bicyclo[2,2,1]hept-5-ene



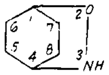
127. Bicyclo[2,2,1]hept-7-ene



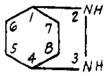
128. B_3 IV (331)



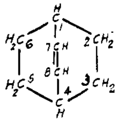
129. Nortropidine



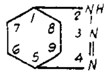
130. B_3 III, 330



131. B_3 IV, 838

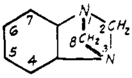


132. Bicyclo[2.2.2]oct-7-ene

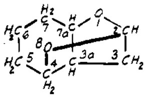


133. p-Benzenediazoimide

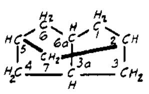
Class C II



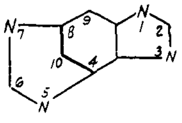
134. B_3 IV, 567



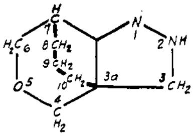
135. B_3 III, 596



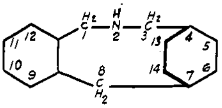
136. C.A. 17, 751



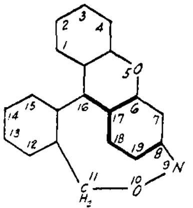
137. B_3 IV (1274)



138. C.A. 17, 2704

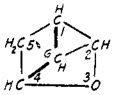


139. B_3 II (1096)

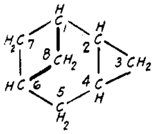


140. B_3 III (575)

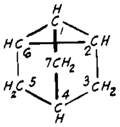
Class C III



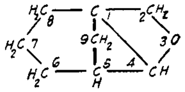
141. B_3 I (266)



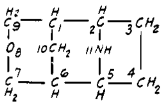
142. C.A. 8, 101



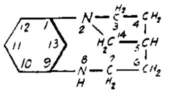
143. Tricyclo[2,2,1,$0^{2,6}$]heptane



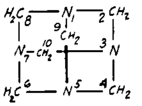
144. B_3 III (460)



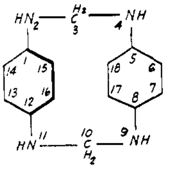
145. B_3 III (613)



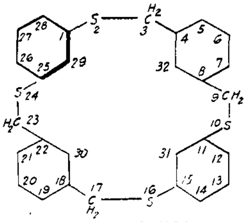
146. B_3 IV, 606



147 Hexamethylenetetramine

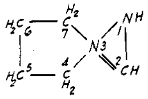


148 C.A. 17, 3863

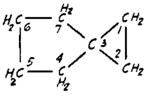


149. C.A. 18, 1996

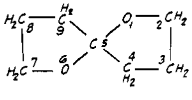
Class D I



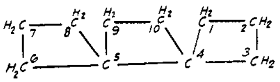
150. B_3 IV, 958



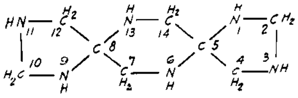
151. os-Spiroheptane



152. Oxetone

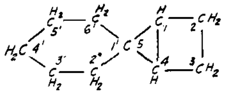


153. C.A. 8, 323 (XX)

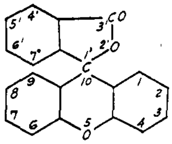


154. C.A. 4, 2646

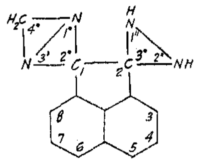
Class D II



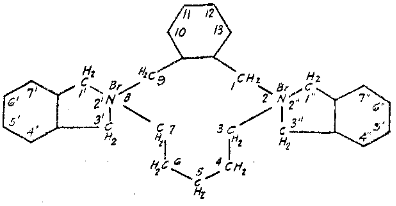
155. C.A. 13, 2016 (VI)



156. Fluoran



157. B_3 III (291) (?)



158 B_3 IV (577)

Xenia, Ohio

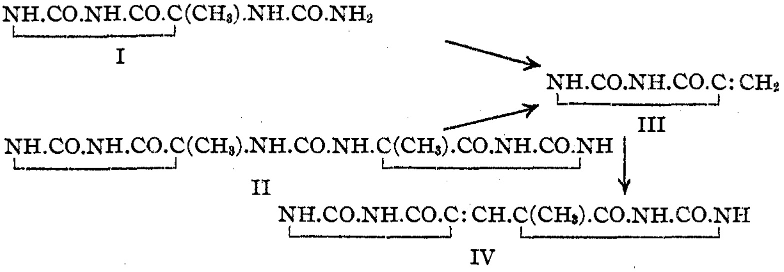
[Contribution from the Department of Chemistry, Yale University]

RESEARCHES ON HYDANTOINS. XLV. DIPYRUVIC UREIDE[1]

By David Davidson and Treat B. Johnson

Received November 11, 1924 Published February 5, 1925

In a previous paper[2] from this Laboratory it has been shown that pyvuril (homo-allantoin) I and dipyruvic triureide II are transformed when heated with strong mineral acids to methylene-hydantoin III. In the absence of reagents which attack the methylene group, the latter undergoes polymerization giving dipyruvic ureide IV.



$$\underbrace{NH.CO.NH.CO.C}(CH_3).NH.CO.NH_2 \quad \text{I}$$

$$\underbrace{NH.CO.NH.CO.C}(CH_3).NH.CO.NH.\underbrace{C(CH_3).CO.NH.CO.NH} \quad \text{II}$$

$$\longrightarrow \underbrace{NH.CO.NH.CO.C}:CH_2 \quad \text{III}$$

$$\downarrow$$

$$\underbrace{NH.CO.NH.CO.C}:CH.\underbrace{C(CH_3).CO.NH.CO.NH} \quad \text{IV}$$

The present paper deals with a study of some of the chemical properties of dipyruvic ureide IV and a consideration of the mechanism of its formation by polymerization of the hydantoin III.

Gabriel[3] who first recognized the true nature of dipyruvic ureide IV obtained it in the bromination of 5-methyl-hydantoin VI. According to his conception of the reaction this product results from a complex process, the final step of which is the direct condensation of bromopyruvic ureide V with 5-methyl-hydantoin VI as expressed below.

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[1] Constructed from part of a dissertation presented by David Davidson to the Faculty of the Graduate School of Yale University in June, 1924, in candidacy for the degree of Doctor of Philosophy.

[2] Davidson, This Journal, 47, 255 (1925).

[3] Gabriel, *Ann.*, 348, 50 (1906).