

A BRIEF INTRODUCTION  
TO THE USE OF  
BEILSTEIN'S HANDBUCH  
DER  
ORGANISCHEN CHEMIE

BY  
ERNEST HAMLIN HUNTRESS, PH.D.  
*Professor of Organic Chemistry  
Massachusetts Institute of Technology*

SECOND EDITION

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**BOOKS BY E. H. HUNTRESS**

Organic Chlorine Compounds.  
Brief Introduction to Use  
of Beilstein's Handbuch der  
Organischen Chemie. Second Edition

**BY E. H. HUNTRESS AND S. P. MULLIKEN**

Identification of Pure Organic  
Compounds. Order 1

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## PREFACE TO THE SECOND EDITION

Since the original publication of this pamphlet, twenty-seven more volumes of Beilstein have appeared completing (1938) both the main and first supplementary series for compounds of established structure in the acyclic, isocyclic and heterocyclic divisions. There remains still unpublished a large section of material dealing with compounds of natural origin whose structure was unknown in 1920; but since these will be mainly of interest to specialists in the several fields the Fourth Edition of Beilstein's *Handbuch* may be regarded as complete to 1920 for all ordinary purposes. This point in the history of the work is particularly interesting and timely since 1938 marks the centennial anniversary of the birth of Friedrich Konrad Beilstein (1838-1906) its founder. For interesting biographical accounts of his life see Ber. **40**, 5041-5078 (1907); J. Chem. Soc. **99**, 1646-1649 (1911); also various papers to be published in 1938 in observance of the centennial celebration.

Apropos of the general applicability of the Beilstein plan as a method of classification (cf. preface to first edition p. vii), the author has personal knowledge that the research laboratory of at least one large industrial organization engaged in the manufacture of organic chemicals has developed a filing code based entirely on the Beilstein system. This code is used for filing all samples of organic compounds, and also for classifying and filing patents, research reports, correspondence and miscellaneous information relating to organic substances.

In the second edition of this pamphlet the original intention to keep its content as brief as consistent with adequate clarity has constantly been kept in mind. The author has brought up to date the charts comprising the nucleus of the exposition and has inserted some new text, particularly with respect to the treatment of heterocyclic compounds. The original very brief list of drill problems has been replaced by a more generous selection of type questions. Opportunity has been taken to correct certain typographical errors and the author acknowledges his gratitude to those who so kindly called them to his attention.

ERNEST H. HUNTRESS

January 1, 1938

## PREFACE TO THE FIRST EDITION

This pamphlet is intended as a brief explanation of the method of classification of organic compounds used in the fourth edition of Beilstein's *Handbuch der Organischen Chemie*. Its primary purpose is to provide in English an elementary exposition of the comprehensive and useful system developed by Prager and Jacobson for the latest edition of the "organic chemist's Bible." It is not intended to include a treatment of the more extensive ramifications of the plan, because these are available in the original to those adequately prepared with the fundamentals. Furthermore, in the interests of simplicity and of brevity the subject matter of this account is restricted to those portions of the classification for which the corresponding volumes have already been published.

The material from which the present brochure is constructed has been used by the author since 1924 as a part of a course of lectures on the use of chemical literature given to students specializing in chemistry at the Massachusetts Institute of Technology. In response to numerous requests from colleagues and former students the substance of the material on the use of Beilstein's *Handbuch* was first arranged for publication as a journal article, but in order to render it more generally available and to provide a convenient form for its users, it was decided to issue it in pamphlet form.

Published material on the Prager-Jacobson classification is meager and most of it is in foreign tongues. A sketch of the evolution of Beilstein's *Handbuch* from its earliest conception has been published by P. Jacobson<sup>1</sup> but this paper does not purport to explain the new classification system adopted for the fourth edition. Richter,<sup>2</sup> editor of the supplementary volumes, has briefly described certain aspects of the plan but his viewpoint is far too advanced for the novice. An extensive treatment of the principles is given in many pages of fine print in the first volume of the work.<sup>3</sup> This same introduction in slightly amended form constitutes a

<sup>1</sup> *Naturwissenschaften*, **7**, 222-225 (1919).

<sup>2</sup> *Z. angew. Chem.*, **38**, 1096-8 (1925).

<sup>3</sup> Beilstein's *Handbuch der Organischen Chemie*, 4th Edition: Vol. 1, pp. 1-47. J. Springer, Berlin, 1918.

part of an entire book<sup>1</sup> recently published by the German Chemical Society, but both of these treatments, though of value to the initiated, are far too comprehensive for elementary instruction. MacArdle<sup>2</sup> has published a much abridged translation of the introductory material from Volume I together with a chart indicating the broad groups of the system. Of the recent books on the use of chemical literature Crane and Patterson<sup>3</sup> dismiss the subject in a paragraph, while Mellon<sup>4</sup> reproduces MacArdle's chart with additions to indicate the recently published volumes.

Inasmuch as Beilstein's *Handbuch* must be used in the German it appears generally to have been inferred that he who could read the system could also read the explanation which preceded it. This assumption, however, is not supported by experience, for even students whose ability to cope with the German introduction is very meager will be found to have little difficulty with the technical vocabulary of the main part of the work. Furthermore, the magnitude of the classification is such that some explanation of the main plan is desirable before the significance of its details can be appreciated. The main purpose of this pamphlet is to present the fundamentals of the scheme of classification in such a form that its students can obtain a sort of aerial view of the plan before proceeding with its details. For this reason many interesting and intrinsically important phases have necessarily been omitted or restricted in scope of treatment.

To the group to which this exposition will be of interest or utility it seems hardly necessary to make any representations concerning the desirability of facility in the use of Beilstein's *Handbuch*. Two relevant circumstances, however, merit a word of comment. The first circumstance arises from the lack of any general index to the compounds included in the system. This implies no lack of diligence on the part of the compilers but is merely a consequence of the magnitude of the plan. Of course each individual volume which has appeared has its own index and the recent publication of the German Chemical Society already referred to has indexes of trivial

<sup>1</sup> *System der Organischen Verbindungen: Ein Leitfaden für die Benutzung von Beilstein's Handbuch der Organischen Chemie* (An Introduction to the Use of Beilstein's Handbook of Organic Chemistry). Deutschen Chemischen Gesellschaft, 1929, 246 pages. Published by J. Springer, Berlin.

<sup>2</sup> Chem. Met. Eng., **22**, 256-8 (1921).

<sup>3</sup> Crane and Patterson: *A Guide to the Literature of Chemistry*. John Wiley & Sons, New York, 1927.

<sup>4</sup> Mellon: *Chemical Publications*. McGraw-Hill, New York, 1928.

names and of classes, but no general detailed index of compounds can be available until completion of the publication of the main work. Thus some knowledge of the classification is required merely to determine whether a given compound has yet been reached in the volumes already published. Furthermore, since some 200,000 substances are included in the fourth edition and each of these has several possible names, *it is often actually more convenient to locate an individual from a knowledge of the systematic arrangement than from the indexes of the separate volumes.*

The second circumstance is that a tested plan for filing current literature about particular compounds is provided which is sufficiently comprehensive to allow for a wide diversification of interests and yet assure complete correlation of the many types of individual compounds. Inasmuch as the number of abstracts annually printed in the organic section (10) of Chemical Abstracts has increased 383 per cent from 1918 to 1928 it is evidently in the interests of individual efficiency to adopt some system of classification of this contemporaneous material which will enable one's fields of interest to be kept constantly up to date and yet which will fall into line with all present facilities. The personal experience of the author has convinced him that adaptation of the Beilstein classification to the arrangement of general subjects rather than individual compounds can readily be made to suit the requirements of the individual. These comments regarding the utility of the plan for the filing of current publications merely show one way in which a knowledge of the plan is convenient. The facile use of the Beilstein classification in the daily work of the laboratory will constitute an adequate objective for most readers.

For advice and suggestions in the preparation of this pamphlet the author is indebted to many colleagues and former students. Sincere acknowledgment of particular aid is due to Professor A. A. Morton, Dr. A. A. Ashdown, Dr. R. C. Young, and to Messrs. I. S. Cliff, G. P. Standley, E. B. Hershberg, and C. D. May.

ERNEST H. HUNTRESS.

*February, 1930.*

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# A BRIEF INTRODUCTION TO THE USE OF BEILSTEIN'S HANDBUCH

## CHAPTER I

### INTRODUCTION

The fourth edition of Beilstein's *Handbuch* is intended to represent a complete survey of the literature to January 1, 1910, of all organic compounds which have been analyzed or otherwise definitely characterized, except materials such as carbon monoxide, carbon dioxide, metallic carbonates, and a few carbides, which have already been included in reference works on inorganic chemistry. Furthermore those natural products which have been extensively investigated are included in the treatment even though they are mixtures of somewhat indefinite character (e.g. essential oils) or are compounds whose exact structure is undetermined (dyes — proteins, etc.). On the other hand, artificial products which are not chemical individuals (such as the phenol-formaldehyde resins) are not discussed except for a brief notation under the head of the parent substance.

The material thus included represents some 200,000 entries and was originally expected<sup>1</sup> to require about fifteen volumes. Although in 1925 Richter predicted<sup>2</sup> eighteen volumes the record of compounds of definite structure alone has actually required twenty-seven, the last of which will be published by 1938. In order to cope with the increasing flood of chemical publication it is planned to issue a series of supplementary volumes each of which will correspond in content to that of the main work but which will cover a period beginning where the main work stops. By 1938, the first twenty-seven of these had appeared, bringing the survey of literature of compounds within their scope

<sup>1</sup> Beilstein, 4th Edition, Volume I, page xiii.

<sup>2</sup> Z. angew. Chem. **38**, 1096 (1925).

to January 1, 1920.<sup>1</sup> A second supplementary series to cover the literature from 1920 on has already been authorized by the German Chemical Society.<sup>2</sup>

The volumes of the main series, therefore, contain only compounds described in the chemical literature before January 1, 1910. Those of the first supplementary series contain important additional data on many of the foregoing and also include substances first described in the literature between January 1, 1910 and January 1, 1920. Except for a generous number of footnotes interjected by the editorial board, data whose origin is more recent than January 1, 1920 does not appear and must await the publication of subsequent series of supplementary volumes.

Searchers should always consult both the main and corresponding supplementary volumes. The location in a supplementary volume of a compound once found in the main series is facilitated by making use of the bold-face type designations of the corresponding main-volume page numbers which appear at the top of each page in the supplements. Thus if a compound is found in Vol. V, page 351 of the main series, one has only to look for V-351 in bold-face type on the page tops of Supplementary Volume V. Where several supplementary volumes are contained in one binding care must be taken to read the volume number correctly.

<sup>1</sup> For tabular outline of content of published volumes see Chart 4. (Pages 31-33.)

<sup>2</sup> Ber. **61A**, 53 (1928).

## CHAPTER II

### THE MODE OF FORMATION OF THE FOUR MAIN DIVISIONS

This system is founded upon the premise that every definite compound can be expressed in a structural formula.<sup>1, 2</sup> Three of the main **Divisions** are based on the type of this formula: the fourth includes natural products of indefinite composition or incompletely known structure. The position of each definite organic compound in the first three divisions is determined by its **stem nucleus**. The stem nucleus is obtained by replacing in the formula of the compound all other atoms or groups attached to carbon by the equivalent number of hydrogen atoms except where such replacement would involve breaking a cyclic chain. This is illustrated in Chart 1. (Pages 4-5.) Furthermore, whenever a given formula gives rise to stem nuclei of more than one division it is assigned a place in the same main division as the one of its component stem nuclei which comes last in the systematic arrangement. This principle, also illustrated in Chart 1, is called "the principle of latest position in the system" and is frequently invoked in similar ambiguous cases throughout the general classification.

The prescription that no cyclic chain of atoms shall be broken during the formulation of the stem nucleus leads to an important difference between the Prager-Jacobson classification and that which was employed in the preceding edition of the *Handbuch*. Considered without reference to the ease with which their cycles of atoms may be opened by the action of reagents, there are many substances which may be considered as heterocyclic from a formal viewpoint which would not be so considered from a practical

*(Continued on page 6)*

<sup>1</sup> Compounds described in the literature prior to 1910 (or 1920) but whose structure has been definitely established only since that time are listed according to the (newly) established formula and usually accompanied by an explanatory footnote with appropriate literature references.

<sup>2</sup> On the other hand in some cases where supposedly established structures are now seriously doubted, the material is regarded as a transformation product of and listed under whichever of its component raw materials comes latest in the system.

## CHART 1

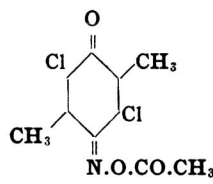
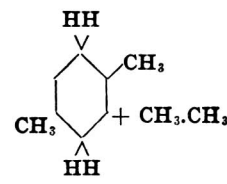
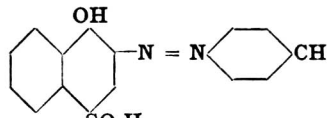
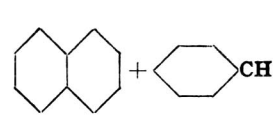
## FORMATION OF THE FOUR MAIN DIVISIONS

(with examples illustrating also the principle of latest position in the system)

**DIVISION I: ACYCLIC STEM NUCLEI.** The carbon atoms are joined in open chains only.

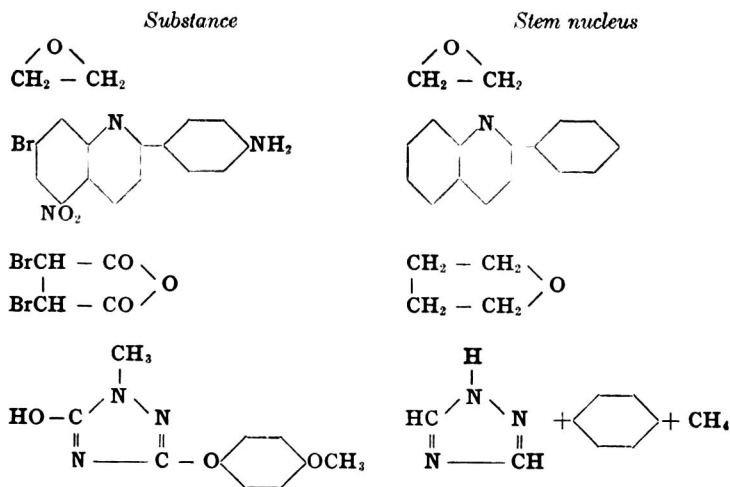
<i>Substance</i>	<i>Stem nucleus</i>
$\text{Br} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2$	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_3$
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}_3$	$\text{CH}_3 \cdot \text{CH}_3 + \text{CH}_3 \cdot \text{CH}_3$
$\text{CH}_3 \cdot \text{CO} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$	$\text{CH}_3 \cdot \text{CH}_3 + \text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_3$
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{SO}_2 \cdot \text{OH}$	$\text{CH}_3 \cdot \text{CH}_3$
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{N} \begin{array}{l} / \text{N} \\ \parallel \\ \backslash \text{N} \end{array}$	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_3$
$(\text{CH}_3)_2 \cdot \text{N} \cdot \text{N} \cdot (\text{CH}_3)_2$	$\text{CH}_4 + \text{CH}_4$

**DIVISION II: ISOCYCLIC STEM NUCLEI.** The carbon atoms are joined in closed rings which *do not* include other kinds of atoms as ring components.

<i>Substance</i>	<i>Stem nucleus</i>
$\begin{array}{c} \text{CH}_3 \quad \quad \text{H} \\ \quad \quad \diagdown \quad / \\ \quad \quad \text{C} \\ \quad \quad / \quad \diagdown \\ \text{CH}_2 \quad \quad \text{CH}_2\text{Cl} \end{array}$	$\begin{array}{c} \text{CH}_2 \quad \quad \text{H} \\ \quad \quad \diagdown \quad / \\ \quad \quad \text{C} \\ \quad \quad / \quad \diagdown \\ \text{CH}_2 \quad \quad \text{CH}_3 \end{array}$
	
$\text{Br} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{Cl}$	$\text{C}_6\text{H}_5 \cdot \text{CH}_3 + \text{CH}_3 \cdot \text{CH}_3$
	

**DIVISION III: HETEROCYCLIC STEM NUCLEI.** The carbon atoms are joined in closed rings which *do* include one or more other kinds of atoms as ring components. Note that the anhydrides and imides of dibasic acids, as well as lactones and lactams, are thus included in this division.

CHART 1 (Continued)



**DIVISION IV: NATURAL PRODUCTS NOT ASSIGNED PLACES IN THE PRECEDING DIVISIONS.**

- Hydrocarbons** petroleum — carotene, etc.
- Ethereal oils**
- Sterols** ergosterol — phytosterol — cholesterol, etc.
- Fatty oils and fats**
- Waxes**
- Resins, balsams, and plant juices** amber — copal — turpentine — caoutchouc — storax — guttapercha — etc.
- Carbohydrates** natural polysaccharides — lactose — maltose — sucrose — starch — cellulose — galactans — glycogen, etc.
- Glucosides** Coniferin — salicin — saponin — amygdalin — convolvulin — cerebrosides — tannin — etc.
- Alkaloids** muscarine — morphine — codeine — brucine — strychnine — spermine, etc.
- Phosphatides** lecithin, etc.
- Proteins** edestin — gliadin — animal albumins and globulins — albumoses — nucleic acids, etc.
- Enzymes**
- Nitrogen-free substances not in preceding groups** asphalt — xanthophyll — graphitic acid — cork — lignin — etc.
- Nitrogenous substances not in preceding groups** chlorophyll — litmus — bilirubin, etc.
- Natural substances not previously classified** humic substances, etc.

standpoint. Thus the anhydrides and imides of dibasic acids whose carboxyl groups are attached to adjacent carbons; sulfimides of analogous compounds with closely adjacent carboxyl and sulfonic acid groups; lactids and lactones of hydroxy acids; lactams of amino acids; sultones of hydroxy-sulfonic acids; sultams of amino-sulfonic acids; and certain cyclic polymers such as paraldehyde, are classified as heterocyclic compounds and therefore listed in Division III. This procedure has caused deferred consideration of many important substances which formerly were arranged with the simple parent compounds.

**SUBCLASSIFICATION OF DIVISION III.** Although the stem nuclei of the Acyclic and Isocyclic Divisions contain only carbon and hydrogen, those of the Heterocyclic Division include also other kinds of atoms as components of the cycle, thus necessitating the establishment of some arbitrary sequence of subclassification. This is effected according to the kind and number of such hetero atoms. Since the most important heterocyclic compounds are those which contain either hetero oxygen or hetero nitrogen (or both) these are listed first. The entire sequence is given in Chart 1-A.

Compounds with sulfur, selenium or tellurium as hetero atoms are regarded as replacement derivatives of the corresponding oxygen heterocycles. They are therefore listed following these substances (cf. page 25) and no special subdivisions for these elements are required.

The further subclassification of these heterocyclic subdivisions into classes, subclasses, rubrics, etc., is effected according to the usual methods employed for the Acyclic and Isocyclic Divisions. (cf. page 18.)



## CHART 1-A

SEQUENCE OF SUBDIVISIONS OF DIVISION III. (HETEROCYCLES)<sup>1</sup>

Compounds with	1 cyclic	O atom (or S, Se, Te)		
" "	2 "	O atoms		
" "	3 "	O "		
" "	4 "	O "		
" "	5 "	O "		
" "	6 or more cyclic	O "		
Compounds with	1 cyclic	N atom		
" "	2 "	N atoms		
" "	3 "	N "		
" "	4 "	N "		
" "	5 or more cyclic	N "		
Compounds with	1 cyclic	O atom and also	1 cyclic	N atom
" "	2 "	O atoms	" "	" "
" "	3 "	O "	" "	" "
" "	4 "	O "	" "	" "
" "	5 or more cyclic	O "	" "	" "
Compounds with	1 cyclic	O atom and also	2 cyclic	N atoms
" "	2 "	O atoms	" "	" "
" "	3 "	O "	" "	" "
" "	4 or more cyclic	O "	" "	" "
Compounds with	1 cyclic	O atom and also	3 cyclic	N atoms
" "	2 "	O atoms	" "	" "
" "	3 "	O "	" "	" "
" "	4 or more cyclic	O "	" "	" "
Compounds with	1 cyclic	O atom and also	4 cyclic	N atoms
" "	2 "	O atoms	" "	" "
" "	3 "	O "	" "	" "
" "	4 or more cyclic	O "	" "	" "

Compounds with 5 or more cyclic N atoms and also cyclic O (S, Se, Te)  
 Compounds with heterocyclic atoms other than O, S, Se, Te, or N.

<sup>1</sup> Cf. also Chart IV (pages 31-33).

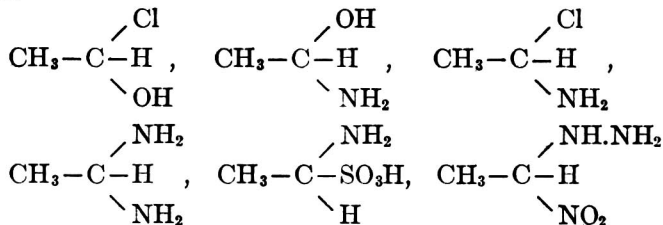
## CHAPTER III

### THE SUBCLASSIFICATION OF DIVISIONS (OR HETEROCYCLIC SUBDIVISIONS)

**THE TWENTY-EIGHT FUNCTIONING CLASSES WITHIN EACH DIVISION.** Division I (acyclic) and Division II (isocyclic) are each further subdivided into **28 Classes**.<sup>1</sup> The first class consists of the stem nuclei themselves. Each of the other 27 classes, however, is characterized by the possession of a group containing at least one replaceable hydrogen atom which may be conceived to be substituted by other atoms or radicals. This characteristic leads to the term **functioning classes** and a list is given in Chart 2. (Pages 10–11.) It should be noted that for reasons which will duly appear the functioning group of Classes 3 and 4 (carbonyl compounds and carboxylic acids, respectively) may, whenever desired, be construed as possessing the hydrated form indicated in the chart. The determination of the particular class to which a given compound belongs is imperative and will be facilitated by the four following rules:

**RULE 1.** Compounds which have a functioning group together with one or two other functioning or non-functioning<sup>2</sup> groups attached to the same carbon atom are considered as derivatives of the =CO compound or –COOH acid which results from the replacement of all these substituents by OH with the subsequent splitting out of water.

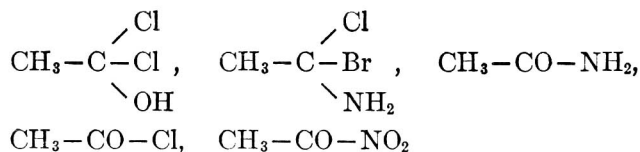
Thus:



are all derivatives of  $\text{CH}_3-\text{CHO}$  in Division I, Class 3.

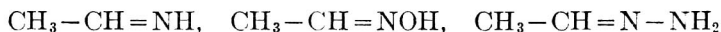
<sup>1</sup> The arbitrary subdivision of Division IV is indicated in Chart 1. Division III (heterocyclic) is arranged in subdivisions according to the kind and number of heterocyclic atoms (cf. Chart 1-A, page 7) and each of these subdivisions is divided into the 28 classes mentioned above.

<sup>2</sup> The seven non-functioning groups are so called because they have no replaceable hydrogen: –F, –Cl, –Br, –I, –NO, –NO<sub>2</sub>, and –N<sub>3</sub> (azido).

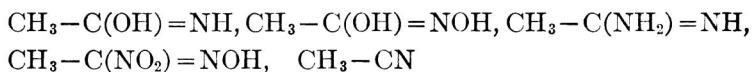


are all derivatives of  $\text{CH}_3-\text{COOH}$  in Division I, Class 4.

**RULE 2.** The same principle applies to the case of nitrogen attached by 2 or 3 valences to a single carbon atom.

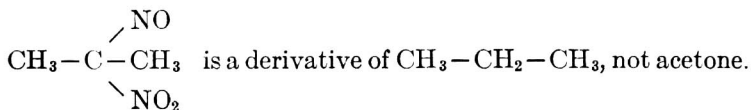
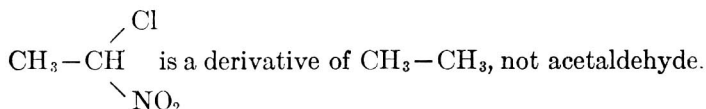


are derivatives of  $\text{CH}_3-\text{CHO}$ .



are derivatives of  $\text{CH}_3-\text{COOH}$ .

**RULE 3.** However, when 2 or 3 *non-functioning* groups are attached to the same carbon without any functioning group being attached as well, rules 1 and 2 do not apply.



**RULE 4.** In Classes 23–28 no metallic compound which can be conceived to be a salt is included. Furthermore, since all alkali metal compounds are construed as salts these metals are omitted from Class 27.

**THE FORMATION OF SUBCLASSES.** The three simplest types of subclassification will be successively illustrated by a discussion of Classes 1, 2, and 3. The mode of combination of a given class with all those preceding will then be further illustrated with Class 4.

According to diminishing saturation.

**CLASS 1. Stem nuclei.** Since this class contains no functioning group it is subclassed according to the decreasing saturation of the several series of stem nuclei which it includes, thus:

(Continued on page 12)

## CHART 2

## THE TWENTY-EIGHT FUNCTIONING CLASSES

1. Stem nuclei	
<hr/>	
2. Hydroxy compounds	-OH
3. Carbonyl compounds	=O( $\begin{matrix} \text{OH} \\ \diagdown \\ \text{OH} \end{matrix}$ )
4. Carboxylic acids	=O(OH)( $\begin{matrix} \text{OH} \\ \diagdown \\ \text{OH} \\ \diagdown \\ \text{OH} \end{matrix}$ )
<hr/>	
5. Sulfinic acids	-SO <sub>2</sub> H
6. Sulfonic acids	-SO <sub>3</sub> H
7. Seleninic and selenonic acids	-SeO <sub>2</sub> H & -SeO <sub>3</sub> H
<hr/>	
8. Amines	NH <sub>2</sub>
9. Hydroxylamines	-NHOH
<hr/>	
10. Hydrazines	-NH.NH <sub>2</sub>
11. Azo compounds	-N:NH
12. Hydroxy hydrazines	-N(OH)NH <sub>2</sub> or -NH.NH(OH)
13. Diazonium, diazo, and isodiazocompounds	-N.OH or -N:N.OH     N
14. Azoxy substances	-N.N.H or -N:NH or -N:NH $\begin{matrix} \diagdown & & \diagup \\ & \text{O} & \\ \diagup & & \diagdown \end{matrix}$ $\begin{matrix} \text{O} \\    \\ \text{O} \end{matrix}$ or $\begin{matrix} \text{O} \\    \\ \text{O} \end{matrix}$ or $\begin{matrix} \text{O} \\    \\ \text{O} \end{matrix}$
15. Nitramines -NH.NO <sub>2</sub>	$\begin{matrix} \text{O} \\    \\ \text{O} \end{matrix}$
Isonitramines	-N=NOH or -N:N $\begin{matrix} \text{O} \\    \\ \text{O} \end{matrix}$ or -N-N-OH $\begin{matrix} \diagdown & & \diagup \\ & \text{O} & \\ \diagup & & \diagdown \end{matrix}$ $\begin{matrix} \text{O} \\    \\ \text{O} \end{matrix}$
<hr/>	
16. Triazanes	-NH.NH.NH <sub>2</sub> or -N $\begin{matrix} \text{NH}_2 \\ \diagdown \\ \text{NH}_2 \end{matrix}$

## CHART 2 (Continued)

17. Triazenes  $-N:N.NH_2$  or  $-NH.N:NH$  or  $-N$   $\begin{array}{l} \text{NH} \\ | \\ \text{NH} \end{array}$
18. Hydroxytriazenes  $-N:N.NHOH$  or  $-N(OH).N:NH$  or  $-NH.N:N.OH$
19. Azoamino oxides  $-N.N.NH_2$  or  $-NH.N.NH$  or  $\begin{array}{c} \diagdown \\ \text{O} \\ \diagup \end{array} -N:N.NH_2$  or  $\begin{array}{c} \diagdown \\ \text{O} \\ \diagup \end{array} -NH.N:NH$  or  $\begin{array}{c} \text{O} \\ || \\ \text{O} \end{array}$
- 
20. Tetrazanes  $-NH.NH.NH.NH_2$  or  $-N(NH_2).NH.NH_2$
21. Tetrazenes  $-NH.N:N.NH_2$  or  $-N:N.NH.NH_2$  or  $-NH.NH.N:NH$  or  $-N.N:NH$   $\begin{array}{c} | \\ NH_2 \end{array}$
22. Substances with N chains of more than four nitrogen atoms.
- 
23. Substances with C bound to element of 5th group: P, As, Sb, Bi (but not N).
24. " " " " 4th " : Si, Ge, Sn, Pb.
25. " " " " 3rd " : B, Al, Tl.
26. " " " " 2nd " : Be, Mg, Ca, Zn, Cd, Hg.
27. " " " " 1st " : Au.
28. " " " " 8th " : Pt.
- 

This complete list is given for reference: in common practice the classes most frequently met are 1-11 inclusive.

## THE SEVEN NON-FUNCTIONING GROUPS (Substituents)

The seven non-functioning substituents are  $-F$ ,  $-Cl$ ,  $-Br$ ,  $-I$ ,  $-NO$ ,  $-NO_2$  and  $-N_3$  (azido).

- Division I. Acyclic compounds  
 Class 1. Stem nuclei  
 Subclass A. Saturated  $C_nH_{2n+2}$   
 " B. Unsaturated  $C_nH_{2n}$   
 " C. Unsaturated  $C_nH_{2n-2}$   
 " D. Unsaturated  $C_nH_{2n-4}$   
 " E. Unsaturated  $C_nH_{2n-6}$

- Division II. Isocyclic compounds  
 Class 1. Stem nuclei  
 Subclass A. Saturated  $C_nH_{2n}$   
 " B. Unsaturated  $C_nH_{2n-2}$   
 " C. Unsaturated  $C_nH_{2n-4}$   
 .....

*Note:* In this division the subclasses run as high as  $C_nH_{2n-78}$

**According to number of characteristic functioning groups.**

**CLASS 2. Hydroxy compounds.** Here a functioning group is present and the subclasses are determined by the number of such groups in the molecule, thus:

- Division I. Acyclic compounds  
 Class 2. Hydroxy compounds  
 Subclass A. Monohydroxy compounds  
 " B. Dihydroxy compounds  
 " C. Trihydroxy compounds  
 .....  
 " J. Nonhydroxy compounds

- Division II. Isocyclic compounds  
 Class 2. Hydroxy compounds  
 Subclass A. Monohydroxy compounds  
 " B. Dihydroxy compounds  
 " C. Trihydroxy compounds  
 .....  
 etc.

**According to increasing number of characteristic atoms.**

**CLASS 3. Carbonyl compounds.** With this class a further complication must be introduced, viz., combination of the characteristic functioning carbonyl group with the functioning group of the preceding class. In other words, provision must now be made not only for those compounds containing one or more carbonyl groups but also for those containing both carbonyl and hydroxyl. Such compounds with mixed functions are listed after all those with a single type of functioning group have been treated. They are then arranged according to increasing number of atoms characteristic of the functioning groups. This is illustrated as follows:



- Division I. Acyclic compounds  
 Class 3. Carbonyl compounds  
 Subclass A. Monocarbonyl compounds  
 " B. Dicarbonyl compounds  
 " C. Tricarbonyl compounds  
 " D. Tetracarbonyl compounds  
 " E. Hexacarbonyl compounds  
 " F. Hydroxy-carbonyl compounds  
     F<sub>1</sub> Those with 2 atoms of O  
     F<sub>2</sub> Those with 3 atoms of O  
     F<sub>3</sub> Those with 4 atoms of O  
     etc.

- Division II. Isocyclic compounds  
 Class 3. Carbonyl compounds  
 Subclass A. Monocarbonyl compounds  
 " B. Dicarbonyl compounds  
 .....  
 " J. Hydroxy-carbonyl compounds  
     J<sub>1</sub> With 2 atoms of O  
     J<sub>2</sub> With 3 atoms of O  
 .....  
     J<sub>11</sub> With 16 atoms of O

#### Further Illustrations of These Three Methods of Subclassification

**CLASS 4. Carboxylic acids.** The pyramiding which results from combinations of each class with those which have preceded it might reach almost overwhelming proportions as the system proceeds were it not for the fact that many representatives of the more complicated combinations are unknown. By way of further illustration of the principle, however, the arrangement of carboxylic acids is outlined as follows:

- Division I. Acyclic compounds  
 Class 4. Carboxylic acids  
 Subclass A. Monocarboxylic acids  
 " B. Dicarboxylic acids  
 " C. Tricarboxylic acids  
 .....  
 " K. Tetradecarboxylic acids  
 " L. Hydroxy-carboxylic acids  
     L<sub>1</sub> Those with 3 atoms of O  
     L<sub>2</sub> Those with 4 atoms of O  
 .....  
     L<sub>3</sub> Those with 13 atoms of O

- Subclass M. Carbonyl-carboxylic acids  
 M<sub>1</sub> Those with 3 atoms of O  
 .....  
 M<sub>9</sub> Those with 11 atoms of O
- “ N. Hydroxy-carbonyl-carboxylic acids  
 N<sub>1</sub> Those with 4 atoms of O  
 .....  
 N<sub>6</sub> Those with 8 atoms of O
- Division II. Isocyclic compounds  
 Class 4. Carboxylic acids  
 Subclass A. Monocarboxylic acids  
 “ B. Dicarboxylic acids  
 .....  
 “ H. Octacarboxylic acids  
 “ J. Hydroxy-carboxylic acids  
 J<sub>1</sub> Those with 3 atoms of O  
 J<sub>2</sub> Those with 4 atoms of O  
 .....  
 J<sub>9</sub> Those with 11 atoms of O
- “ K. Carbonyl-carboxylic acids  
 K<sub>1</sub> Those with 3 atoms of O  
 .....  
 K<sub>10</sub> Those with 14 atoms of O
- “ L. Hydroxy-carbonyl-carboxylic acids  
 L<sub>1</sub> Those with 4 atoms of O  
 .....  
 L<sub>13</sub> Those with 17 atoms of O.

**SOME PECULIARITIES OF CLASSES 5-28.** From the fifth class (sulfinic acids) on through the system, multiple combinations of a single function form the basis of the first few subclasses, as has already been indicated with the oxygenated functions. The formation of subclasses of mixed functions, however, cannot conveniently be based upon empirical composition as with Class 4. Instead, the further subclasses are obtained by combining the new group with the series of oxygenated functions already determined. This is best understood by an illustration:

- Division I. Acyclic compounds  
 Class 8. Amines  
 Subclass A. Monamines  
 “ B. Diamines  
 “ C. Triamines  
 “ D. Hydroxy-amines  
 D<sub>1</sub> Amino derivatives of monohydroxy compounds  
 D<sub>2</sub> Amino derivatives of dihydroxy compounds  
 .....

- Subclass E. Carbonyl-amines  
 E<sub>1</sub> Amino derivatives of monocarbonyl compounds  
 .....
- “ F. Hydroxy-carbonyl-amines  
 F<sub>1</sub> Amino derivatives of hydroxy-carbonyl compounds with 2 atoms O  
 .....
- “ G. Aminocarboxylic acids  
 G<sub>1</sub> Amino derivatives of monocarboxylic acids  
 G<sub>2</sub> Amino derivatives of dicarboxylic acids  
 .....
- “ H. Amino-hydroxy-carboxylic acids  
 H<sub>1</sub> Amino derivatives of hydroxy-carboxylic acids with 3 O atoms  
 H<sub>2</sub> Amino derivatives of hydroxy-carboxylic acids with 4 O atoms  
 .....

**THE ESTABLISHMENT OF RUBRICS WITHIN THE SUBCLASSES ACCORDING TO DECREASING SATURATION.** It will be recalled that further subclassification of Class 1 where no functioning group was present was effected according to decreasing saturation. This method of subdivision is now employed for the further treatment of the later subclasses themselves. Thus the subclass of monohydroxy alcohols is further divided according to the diminishing saturation of its component series. Two illustrations of this principle are given below:

- Division I. Acyclic compounds  
 Class 2. Hydroxy compounds  
 Subclass A. Monohydroxy compounds  
 Rubric 1. Monohydroxy alcohols  $C_nH_{2n+2}O$   
 “ 2. Monohydroxy alcohols  $C_nH_{2n}O$   
 “ 3. Monohydroxy alcohols  $C_nH_{2n-2}O$   
 “ 4. Monohydroxy alcohols  $C_nH_{2n-4}O$   
 “ 5. Monohydroxy alcohols  $C_nH_{2n-6}O$   
 Subclass B. Dihydroxy compounds  
 Rubric 1. Dihydroxy alcohols  $C_nH_{2n+2}O$   
 .....
- Division II. Isocyclic compounds  
 Class 2. Hydroxy compounds  
 Subclass A. Monohydroxy compounds  
 Rubric 1. Monohydroxy compounds  $C_nH_{2n}O$   
 “ 2. Monohydroxy compounds  $C_nH_{2n-2}O$   
 “ 3. Monohydroxy compounds  $C_nH_{2n-4}O$   
 “ 4. Monohydroxy compounds  $C_nH_{2n-6}O$   
 .....

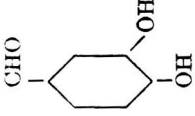
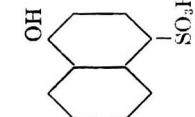
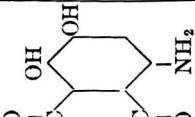
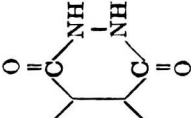
Rubric 24.	Monohydroxy compounds	$C_nH_{2n-48}O$
Subclass B.	Dihydroxy compounds	
Rubric 1.	Dihydroxy compounds	$C_nH_{2n}O_2$
.....	.....	.....
" 24.	Dihydroxy compounds	$C_nH_{2n-14}O_2$

**THE ARRANGEMENT OF RUBRIC MEMBERS INTO GROUPS OF ISOMERS.** The fourth degree of subclassification arranges each rubric into an homologous series of groups of isomers of equal degree of saturation but with increasing number of carbon atoms. This is illustrated as follows:

Division I.	Acyclic compounds
Class 2.	Hydroxy compounds
Subclass A.	Monohydroxy compounds
Rubric 1.	Monohydroxy alcohols $C_nH_{2n+2}O$
Series a.	$CH_4O$ Methyl alcohol
" b.	$C_2H_6O$ Ethyl alcohol
" c.	$C_3H_8O$ The propyl alcohols
" d.	$C_4H_{10}O$ The butyl alcohols
" e.	$C_5H_{12}O$ The amyl alcohols
	etc.

Division II.	Isocyclic compounds
Class 2.	Hydroxy compounds
Subclass A.	Monohydroxy compounds
.....	.....
Rubric 4.	Monohydroxy compounds $C_nH_{2n-6}O$
Series a.	$C_6H_6O$ isomers
" b.	$C_7H_8O$ isomers
" c.	$C_8H_{10}O$ isomers
.....	.....
" k.	$C_{16}H_{26}O$ isomers

**ARRANGEMENT OF GIVEN GROUP OF ISOMERS INTO INDIVIDUAL INDEX COMPOUNDS.** Of course in simple cases like methyl or ethyl alcohols these compounds themselves are **Index Compounds**. With increasing numbers of carbon atoms, however, we have a final subdivision of isomeric groups into individual **Index Compounds**. The order of arrangement within a given group of isomers will not be discussed in this paper, however, as the magnitude of space covered is usually not large and location of the desired isomer quite obvious.

<b>Structural Formula</b>				
<b>Empirical Formula</b>	$C_7H_8O_3$	$C_{10}H_8O_3S$	$C_{14}H_8O_4N$	$C_8H_8O_2N_2$
<b>Division</b>	I; Acyclic	II; Isocyclic	II; Isocyclic	III; Heterocyclic
<b>Subdivision</b> (For heterocycles only)	—	—	—	2 cyclic N atoms
<b>Class</b>	Carboxylic acids	Hydroxy-sulfonic acids	Hydroxy-carbonyl compounds	Carbonyl compounds
<b>Subclass</b>	Dicarboxylic acids	Sulfonic acids of monohydroxy compounds	3 atoms oxygen	Dicarbonyl compounds
<b>Rubric</b>	$C_nH_{2n-6}O_4$	$C_nH_{2n-12}O$ (corresponding monohydroxy compound)	$C_nH_{2n-3}O_3$	$C_nH_{2n-10}O_2N_2$
<b>Series</b>	$C_6$	$C_{10}$	$C_7$	$C_8$
<b>Index compound</b>	Beil. II-803	Beil. XI-271	Beil. VIII-246	Beil. XXIV-371
<b>Name</b>	Muconic acid	Nevile-Winther acid	Protocatechuic aldehyde	Phthalhydrazide

**RÉSUMÉ OF SUBCLASSIFICATION OF DIVISIONS.** The systematic methods of subclassification of Divisions discussed in this chapter may be summarized by expressing the sequence of treatment of an index compound in the following form:

Division	(skeleton)
Subdivision	(kind and number of hetero atoms)
Class	(latest functional group)
Subclass	(number of functional groups or of characteristic atoms)
Rubric	(saturation)
Series	(number of carbon atoms)
Individual	

The use of this "Beilstein hierarchy" is further illustrated by the examples on page 17.



## CHAPTER IV

### THE ARRANGEMENT OF DERIVATIVES OF THE INDIVIDUAL INDEX COMPOUNDS

#### ARRANGEMENT OF DATA ON THE COMPOUND ITSELF.

When the individual index compound is located in the system its properties will be found listed under the following headings:

Structure and configuration — bibliographical citations if there exists special literature in book form — historical notes on particularly important compounds.

Occurrence — formation — preparation.

Properties — color — crystal form — physical constants — etc.

Chemical reactions — those effected by physical means — by inorganic reagents — by organic reagents.

Physiological action.

Uses.

Analytical — detection — testing — determination.

Addition compounds and salts.

Transformation products of unknown structure.

**THE THREE TYPES OF DERIVATIVES.** Apart from these data on the index compound itself there remains to be considered the mode of treatment of the three types of derivatives to which each index compound may give rise. A clear conception of this point is the key to easy use of the Beilstein classification and particular attention should be given to what follows. The three types of derivatives of each index compound are always discussed in the following order:

(1) “**Functional derivatives**” resulting from the replacement of the characteristic hydrogen of the functioning group by (a) organic groups: (b) inorganic groups.

(2) “**Substitution products**” (non-functional derivatives) resulting from the substitution of stem nuclear hydrogen by one or more of the seven non-functioning substituents:  $-F$ ,  $-Cl$ ,  $-Br$ ,  $-I$ ,  $-NO$ ,  $-NO_2$ ,  $-N_3$ .

(3) “**Replacement derivatives**” resulting from the formal replacement of oxygen in a functioning group by sulfur, selenium, or tellurium.

In contemplating the order in which these derivatives are discussed it is helpful to realize that the space devoted to the first

group (functional derivatives) is often very large as compared with that required for the two other types. This arises on one hand from the fact that a functioning hydrogen may be replaced by a group which may itself have a functioning hydrogen which may similarly be substituted, thus:  $C_6H_5-SO_2OH$  may have a functional derivative  $C_6H_5.SO_2.O.CH_2OH$ , and this in turn may give the derivative  $C_6H_5.SO_2.O.CH_2.OCH_3$ , etc., and on the other from the fact that sometimes several functioning hydrogens may be replaced in the original or derived molecule: thus  $C_6H_5NH_2$  yields two series of derivatives,  $C_6H_5.NHCH_3$ , and  $C_6H_5.N(CH_3)_2$ . Furthermore, as the system proceeds the number of organic hydroxyl compounds which precede the given index compound and may thus be coupled with it of course increases rapidly. Thus, the functional derivatives of benzoic acid cover 224 pages whereas the substitution products require but 86, and the replacement derivatives but 10.

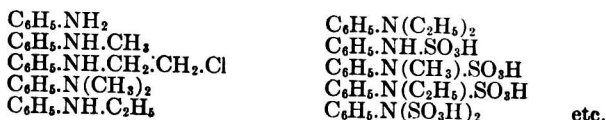
### (1) FUNCTIONAL DERIVATIVES

The concepts of anhydrosynthesis and degree of alteration. These functional derivatives are considered as being formed by "anhydrosynthesis," that is, by coupling of the functioning group (if carbonyl or carboxyl, in the hydrated form) either with organic compounds containing hydroxyl attached to carbon, or with inorganic hydrogen compounds, with consequent elimination of water. The component reacting with the index compound is known as the **coupling compound**. A coupling reaction which eliminates one molecule of water in this way is said to effect a first degree alteration of the index compound. If the coupling compound is itself so constituted that either substitution or further functional alteration may occur, second degree or even higher alterations of the index compound are said to result. It is an important principle of the system that further alteration of a given first degree compound is carried as far as possible before a new first degree derivative is listed. For example:

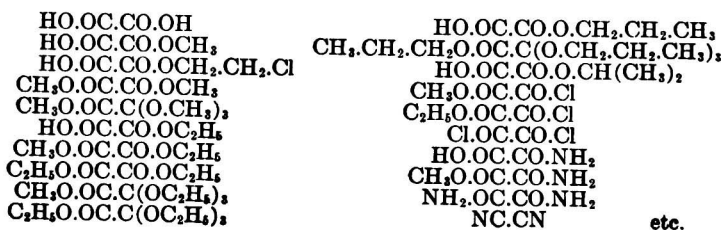
Index compound	Coupling compound	1st degree derivative	2nd degree derivative	3rd degree derivative
$CH_3OH$ $CH_3.CH_2.CH_2.OH$ $CH_3.COOH$ $CH_3.COOH$ $C_6H_5.OH$ $C_6H_5.NH_2$	$HO.CH_3$ $HO.CH_2.CH_3$ $HO.CH_2.CH_2$ $HBr$ $HO.SO_2.OH$ $HO.CH_3$	$CH_3.O.CH_3$ $C_6H_7.O.CH_2.CH_3$ $CH_3.CO.O.C_2H_5$ $CH_3.CO.Br$ $C_6H_5.O.SO_2.OH$ $C_6H_5.NH(CH_3)$ $C_6H_5.N(CH_3)_2$	$C_6H_7.O.CH_2.CH_2.Cl$ $CH_3.CO.O.CH_2.CH_2.NO_2$  $C_6H_5.O.SO_2.NH_2$	$C_6H_5.O.SO_2NH(Cl)$

**Order of coupling compounds.** It is evidently necessary to prescribe a definite order in which the various coupling compounds shall be considered to react with a given index compound. Just as an arbitrary order of functioning classes was indicated in Chart 2 so a similar sequence of coupling compounds is given in Chart 3. (Pages 22-23.) The sequences depicted in the three charts thus given really comprise the essential structure of the system. The various kinds of coupling reactions will now be explained.

**Derivatives of compounds with but one functional group.** The simplest kind of coupling is involved when the index compound has but one functioning group. If this group in turn possesses but one replaceable hydrogen the simple rules already indicated suffice: if this group has more than one replaceable hydrogen some additional regulation is demanded. When more than one first degree alteration is possible in the same compound the procedure is to combine the first additional coupling with all which has preceded it, then make the next similar additional coupling and combine this in turn with all that has preceded it. This is stated briefly in the maxim: "First combine the new with that which has preceded: then multiply the new." For example:



**Derivatives of compounds with two functional groups.** When the index compound possesses two functional groups, however, these groups may be the same or they may be different. In the first case where the groups are alike a first degree alteration is made in one of the like functioning groups and all possible second (or higher) degree alterations are listed for this combination. Then for each of these first degree alteration compounds alteration of the second functioning group is begun and continued in accordance with the series of coupling compounds until the alteration is the same as that of the first group. This is illustrated as follows:



## CHART 3

## ORDER OF ORGANIC AND INORGANIC COUPLING COMPOUNDS

## I. ORGANIC COUPLING COMPOUNDS.

All compounds containing hydroxyl attached to carbon in the order in which they occur in the system. (See Notes below.)

*Note 1.* Only those organic substances are considered as coupling compounds which during the formation of water with the index compound can split out hydroxyl attached to carbon. Thus substances like  $\text{CH}_3\cdot\text{NH}_2$  do not occur in the list.

*Note 2.* Furthermore, not every coupling compound can split out water with every functioning class: e.g., anhydrosynthesis between the index compound  $\text{CH}_3\cdot\text{NH}_2$  and the coupling compound  $\text{HCl}$  is not possible.

*Note 3.* Finally, no functional derivatives obtained by anhydrosynthesis are so listed if it happens that they can be regarded as substitution products or as index compounds. Thus,  $\text{C}_6\text{H}_5\cdot\text{OH} + \text{HCl} = \text{C}_6\text{H}_5\text{Cl} + \text{H}_2\text{O}$  but chlorobenzene is properly listed as a substitution product of benzene. Similarly  $\text{CH}_3\cdot\text{CH}_2\cdot\text{OH} + \text{NH}_3 = \text{C}_2\text{H}_5\cdot\text{NH}_2 + \text{H}_2\text{O}$  but ethyl amine is an index compound in its own right.

*Note 4.* Corresponding to the principle of latest position in the system the coupling of an index compound is effected only with such organic hydroxyl derivatives as have preceded the index compound itself: thus,  $\text{CH}_3\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3$  is a functional derivative of n-butyl alcohol, not of ethanol.

*Note 5.* Beginning with the isocyclic division, however, a general deviation from this principle is made to the extent of regarding corresponding classes of the acyclic and isocyclic divisions as constituting a single class whose members are subclassed according to diminishing saturation. For instance, in listing the functional derivatives of alpha naphthol, all monohydroxy compounds (both acyclic and isocyclic) are taken as coupling compounds in order of diminishing saturation before the acyclic and isocyclic carboxylic acids are similarly considered. Thus:

Methyl naphthyl ether	$\text{C}_{10}\text{H}_7\cdot\text{O}\cdot\text{CH}_3$
Ethyl naphthyl ether	$\text{C}_{10}\text{H}_7\cdot\text{O}\cdot\text{C}_2\text{H}_5$
n-Propyl naphthyl ether	$\text{C}_{10}\text{H}_7\cdot\text{O}\cdot\text{C}_3\text{H}_7$
Isoamyl naphthyl ether	$\text{C}_{10}\text{H}_7\cdot\text{O}\cdot\text{C}_5\text{H}_{11}$
Phenyl naphthyl ether	$\text{C}_{10}\text{H}_7\cdot\text{O}\cdot\text{C}_6\text{H}_5$
(Phenyl-vinyl) naphthyl ether	$\text{C}_{10}\text{H}_7\cdot\text{O}\cdot\text{C}(\text{:CH}_2)\cdot\text{C}_6\text{H}_5$
Dinaphthyl ether	$\text{C}_{10}\text{H}_7\cdot\text{O}\cdot\text{C}_{10}\text{H}_7$
Ethylene glycol dinaphthyl ether	$\text{C}_{10}\text{H}_7\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_{10}\text{H}_7$
.....	.....
Naphthyl acetate	$\text{C}_{10}\text{H}_7\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_3$

## CHART 3 (Continued)

## II. INORGANIC COUPLING COMPOUNDS.

1. Hydrogen peroxide     $\text{HO.OH}$ 

2. Oxygenated acids

Of periodic group 7

- A.  $\text{HO.Cl} - \text{HO.ClO} - \text{HO.ClO}_2 - \text{HO.ClO}_3 - \text{etc.}$   
 B.  $\text{HO.Br} - \text{etc.}$   
 C.  $\text{HO.I} - \text{etc.}$

Of periodic group 6

- D.  $\text{HO.S.OH} - [\text{HO.S(O)H}] - \text{H}_2\text{S}_2\text{O}_4 - \text{HO.SO.OH} -$   
 $[\text{HO.SO}_2\text{H}] - \text{HO.SO}_2\text{.OH}$   
 E.  $\text{HO.Se.OH} - \text{etc.}$

Of periodic group 5

- F.  $\text{HO.N:N.OH} - \text{HO.NO} - \text{HO.NO}_2 - \text{etc.}$   
 G.  $\text{HO.P(OH)}_2 - \text{etc.}$

Of periodic group 4

- H.  $\text{HO.SiO.OH} - \text{etc.}$

3. Halogen hydrides     $\text{HF} - \text{HCl} - \text{HBr} - \text{HI}$ 

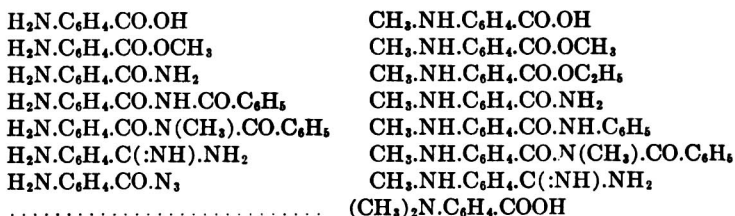
4. Nitrogen compounds whose coupling involves H directly attached to N

- A.  $\text{H}_3\text{N} - \text{H}_2\text{N.OH} - \text{HNO}$  [or the hydrated forms  $\text{H.N(OH)}_2$  or  $\text{H}_2\text{N(O).OH}$ ] —  $\text{H.NO}_2$   
 B.  $\text{H}_2\text{N.NH}_2$  and other di-nitrogen compounds corresponding to the functioning groups of Classes 10–15 (cf. Chart 2, page 10)  
 C.  $\text{H}_2\text{N.NH.NH}_2$  and other tri-nitrogen compounds corresponding to the functioning groups of Classes 16–19  
 D. Nitrogen compounds with more than three N atoms corresponding to the functioning groups of Classes 20–22

5. Compounds of elements of the 5th (e.g., P, As, Sb, Bi), 4th, 3rd, 2nd, 1st, and 8th groups of the periodic system whose coupling involves H directly attached to the element in question: i.e., corresponding to Classes 23–28.

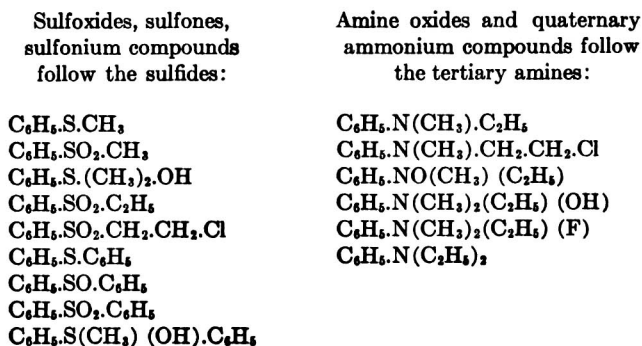
## 24 DERIVATIVES OF THE INDIVIDUAL INDEX COMPOUNDS

In the second case where the two functioning groups in the same index molecule are different the procedure is more simple. That group which stands first in the list of classes (Chart 2) is caused to undergo all possible alterations in orderly sequence; after these have all been considered, alteration of the second group is begun, each first degree alteration of this group being combined with all possible alterations of the first function before another such first degree alteration is contemplated. Thus:



### Derivatives formed by valence change of characteristic element.

A special type of functional derivative is involved when alteration occurs by virtue of a valence change in its characteristic element. The most important cases of this sort are the transition of bivalent sulfur to valences of four or six, and the change of trivalent to pentavalent nitrogen. Such products are regarded as addition products of the corresponding compounds of lower valence, and are listed thereafter. Thus:



In analogy with this rule should be noted the case of poly-valent iodine compounds which are listed directly after the corresponding monovalent iodine substitution product; e.g.,  $\text{C}_6\text{H}_5.\text{I}$ ,  $\text{C}_6\text{H}_5.\text{I}:\text{O}$ ,  $\text{C}_6\text{H}_5.\text{I}:\text{Cl}_2$ ,  $\text{C}_6\text{H}_5.\text{IO}_2$ .

**(2) SUBSTITUTION PRODUCTS**

After all known functional derivatives of an index compound have been discussed the substances formed by replacement of stem nuclear hydrogen by non-functioning substituents, i.e., the substitution products, are listed in an order depending on the following sequence of substituents:  $-F$ ,  $-Cl$ ,  $-Br$ ,  $-I$ ,  $-NO$ ,  $-NO_2$ ,  $-N_3$ . Where only a single type of such substituent is involved the products are obviously listed according to increasing numbers of substituent atoms or groups. Where several types of substituent are present, however, the procedure is summarized in the rule, "The new substituent is combined with all preceding combinations: the amount of the new substituent is then increased with combination of all preceding material at each step." This is illustrated as follows:

$C_6H_5.F$	$C_6H_3(Br)Cl_2$	$C_6H_3(I):Cl_2$
$C_6H_4:F_2(o,m,p)$	$C_6H_2(Br)Cl_3$	$C_6H_5.NO_2$
$C_6H_5.Cl$	$C_6H_4:Br_2(o,m,p)$	$C_6H_4.(NO_2).F$
$C_6H_4.(Cl).F$	$C_6H_3:Br_2(Cl)$	$C_6H_4.(NO_2).Cl$
$C_6H_4:Cl_2(o,m,p)$	$C_6H_3:Br_3$	$C_6H_3.(NO_2):Cl_2$
$C_6H_5.Br$	$C_6H_5.I$	$C_6H_4.(NO_2).Br$
$C_6H_4.(Br).F$	$C_6H_4.(I).F$	$C_6H_3(NO_2).(Br).Cl$
$C_6H_4.(Br).Cl$	$C_6H_4.(I).Cl$	$C_6H_2(NO_2).(Br):Cl_2$

It is especially important to remember that, corresponding to the principle of latest position in the system, those derivatives which result not only by alteration of a functioning group, but by substitution of stem nuclear hydrogen as well, are classified in the later group as substitution products. For example,  $NO_2.C_6H_4.CO.OC_2H_5$  is listed as the ethyl ester of  $NO_2.C_6H_4.CO.OH$  and not under ethyl benzoate as a nitro derivative. Similarly,  $Cl.C_6H_4.CO.OC_2H_5$  is listed later than  $C_6H_5.CO.OC_6H_4.Cl$  because the former is a derivative of a substituted benzoic acid which of course follows benzoic acid itself.

**(3) REPLACEMENT DERIVATIVES RESULTING FROM FORMAL  
REPLACEMENT OF FUNCTIONING OXYGEN BY SULFUR,  
SELENIUM OR TELLURIUM**

Except where groups containing these elements may constitute classes of independent standing, such materials are treated after both the functional derivatives and substitution products have been completely discussed. Thus, although benzene sulfonic acid is a member of Class 6 of the isocyclic division, ethyl mercaptan

$C_2H_5.SH$  is taken up after ethyl alcohol and its functional derivatives and substitution products have been completed and before the propyl alcohols have been begun. These sulfur, selenium, and tellurium analogs may, of course, have functional derivatives and substitution products of their own and these are treated in the usual way.

**DERIVATIVES OF HETEROCYCLIC INDEX COMPOUNDS.** The principles just outlined regarding the mode of formation and sequence of classification of the three types of derivative of an index compound, although introduced by consideration of Divisions I and II, naturally hold also for heterocyclic index compounds (Division III). Here, however, one additional peculiarity must now be mentioned.

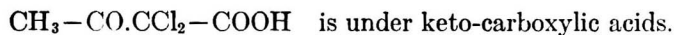
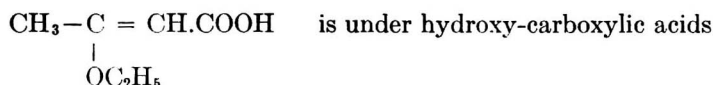
Whereas in Divisions I and II the formation of functional derivatives could involve in the index compound only H attached to C, in the heterocyclic division there are many in which a H attached to N is replaced by another atom or group. For example there are N-alkyl, N-hydroxy, N-aminopyrrolidines as well as the corresponding 2-(or 3-)-C-alkyl (or hydroxy- or amino-) pyrrolidines. In the classification of such compounds the H attached to the heterocyclic N is regarded as a functioning H and its derivatives are construed to be formed (by anhydrosynthesis) in exactly the same fashion as those of the various functioning classes shown in Chart 2. (Pages 10-11.) In other words only such substances of Division III may be regarded as index compounds as have no other atoms or groups except H attached to the hetero nitrogen atom. If in addition to a heterocyclic =N.H group, other functional groups of Chart 2 are also present, the =N.H is regarded for the purpose of classification of derivatives as if it were an amino ( $-NH_2$ ) group. (cf. page 24.)



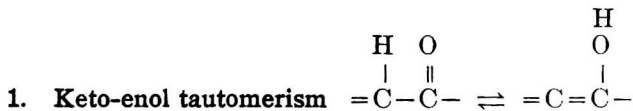
## CHAPTER V

### THE LOCATION OF COMPOUNDS OF TAUTOMERIC STRUCTURE

In the case of compounds which possess two or more tautomeric forms it is usual to designate one of these as the **index formula** and append to it the data on the substance itself. In the position corresponding to the other formula **cross references** are printed if necessary. The data on the desmotropic substance itself is thus located under one definite heading, whether both forms are isolatable or not. Thus the salts of pseudo-acids are listed under the parent substances: e.g., the salts of nitroethane are listed under  $\text{CH}_3\text{CH}_2\text{NO}_2$  even though they are represented by the formula  $\text{CH}_3\text{CH} = \text{NO.OH}$ ; sodium acetoacetic ester under the parent material. However, those derivatives of tautomers whose isomerization is prevented because of replacement of labile hydrogen by other groups are registered in the various places appropriate to their structure, thus

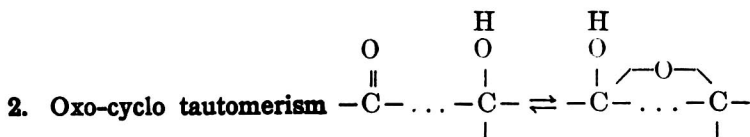
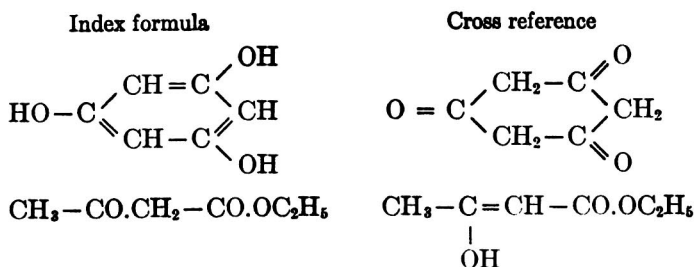


With these fundamental principles covering all types of desmotropic substances it merely becomes necessary to specify under each kind which isomer is to be regarded as the index formula. The seven important types of desmotropes with appropriate rulings are listed below.



The enol form is to be regarded as the index compound whenever (a) it contains the hydroxyl group in an aromatic benzene or pyridine ring, or (b) in a quinoid ring, or (c) in any other aromatic heterocyclic ring provided it is not adjacent to any hetero atom.

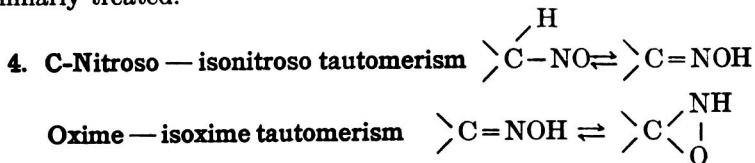
In all cases not covered by the above rule the keto form is the index compound. Thus:



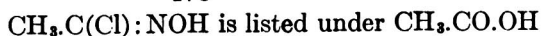
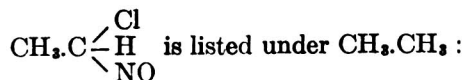
The index formula is usually the keto (open) form.



This case is a complete analog to keto-enol tautomerism and is similarly treated.

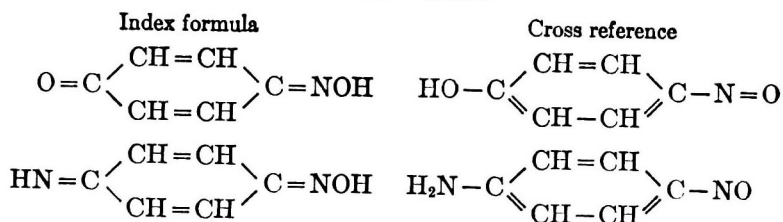


A few true nitroso compounds are known which can be rearranged to definite oximes. Since this is not tautomerism in the usual sense the nitroso compounds are registered as substitution products and the oximes in accordance with the usual procedure. For example:



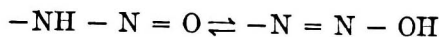
On the other hand there are many isonitroso compounds (oximes of aldehydes, ketones, keto-acids, etc.) which possess no characteristics of true nitroso compounds and these are listed as oximes. In

the particularly important case of nitrosophenols it is emphasized that these are indexed as oximes. Thus:

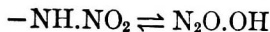


Always indexed under the true nitro form.

6. Nitrosamine — isodiazo tautomerism

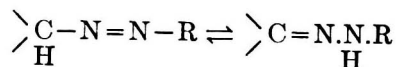


Nitramine — isonitramine — nitrosohydroxylamine tautomerism

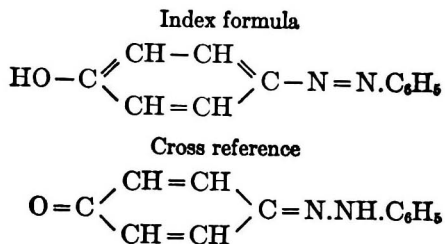


Always indexed under the isodiazo or isonitramine formula.

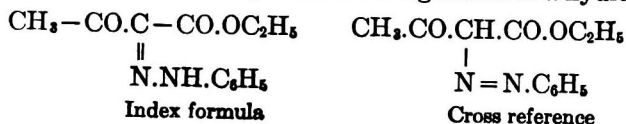
7. Azo-hydrazone tautomerism.



If the compound can be registered either as an aromatic hydroxy-azo or aminoazo compound it is registered under the azo form in accordance with the preceding rule on keto-enol and imino-amino tautomerism. Thus:



In all cases where this is not possible it is registered as a hydrazone:



## CHAPTER VI

### THE METHOD OF FINDING A PARTICULAR COMPOUND FROM ITS STRUCTURAL FORMULA

**THE DETERMINATION OF DIVISION.** The first step toward locating in the system the position of the data for any compound of established structure is to recognize the Division to which it belongs. This is determinable from the stem nucleus or from that one of several component stem nuclei which occurs latest in the system. (cf. pages 4-5.) After a little experience the Division can be established almost instantly by inspection of the formula. This assignment of Division places the first limitation on the volumes where its description is to be expected, thus:

Compounds of Division I (Acyclic)	must be in Vols. I-IV, incl.
“ “ “ II (Isocyclic)	“ “ Vols. V-XVI, incl.
“ “ “ III (Heterocyclic)	“ “ Vols. XVII-XXVII, incl.

**ASSIGNMENT OF CLASS AND SUBORDINATE LOCATION.** Having determined the division the next procedure is to recognize the class under which the individual is discussed. Two types of procedure result at this point according (1) to whether the compound is itself an index compound or (2) is a functional derivative, i.e., whether it can be separated into one or more index compounds and coupling compounds.

**(1) THE SUBSTANCE IS ITSELF AN INDEX COMPOUND (cf. page 21)**

**One functioning group is present.** In the simplest case inspection will suggest the class to which the substance is assigned: thus,  $\text{CH}_3\text{CH}_2\text{SO}_3\text{H}$  belongs in Division I (Acyclic), Class 6 (Sulfonic acids). In case non-functioning substituents are also attached to the same carbon atom as is the functioning group, it should be recalled that Rule 1 (page 8) will apply. Thus,  $\text{C}_6\text{H}_5\text{CH}(\text{Br})(\text{OH})$  is listed under  $\text{C}_6\text{H}_5\text{CHO}$ , benzaldehyde, in Division II (Isocyclic), Class 3 (Carbonyl compounds), and not under benzyl alcohol,  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ . When non-functioning substituents are located on some other carbon than that which bears the functioning group

*(Continued on page 34)*

## CHART 4

## A SURVEY OF THE BEILSTEIN VOLUMES ALREADY PUBLISHED

	System Numbers <sup>1</sup>	Main Series	First Supple- mentary Series
<b>DIVISION I: ACYCLIC</b>			
1. Hydrocarbons . . . . .	1- 15	Vol. I <sup>2</sup> 1918, 983 pp.	Vol. I <sup>2</sup> 1928, 492 pp.
2. Hydroxyl compounds . . . . .	16- 70		
3. Carbonyl compounds . . . . .	71		
Simple and polycarbonyls . . . . .	72-110	Vol. II 1920, 920 pp.	Vol. II 1929, 355 pp.
Hydroxy-carbonyls . . . . .	111-151		
4. Carboxylic acids . . . . .	152		
Mono and polycarboxylic acids . . . . .	153-194	Vol. III 1921, 938 pp.	Vol. III-IV 1929, 662 pp.
Hydroxy-carboxylic acids . . . . .	195-275		
Carbonyl-carboxylic acids . . . . .	276-316		
Hydroxy-carbonyl- carboxylic acids . . . . .	317-322	Vol. IV 1922, 734 pp.	
5. Sulfinic acids . . . . .	323		
6. Sulfonic acids . . . . .	324-331		
7. Seleninic, selenonic acids, etc.	331a	Vol. IV 1922, 734 pp.	
8. Amines . . . . .	332		
Simple and polyamines . . . . .	333-349		
Hydroxy-amines . . . . .	350-356	Vol. IV 1922, 734 pp.	
Carbonyl-amines . . . . .	357-359		
Hydroxy-carbonyl-amines . . . . .	360		
Amino-carboxylic acids . . . . .	361-375	Vol. IV 1922, 734 pp.	
Amino-hydroxy-carboxylic acids . . . . .	376		
Amino-carbonyl-carboxylic acids . . . . .	377		
Amino-sulfinic acids . . . . .	378	Vol. IV 1922, 734 pp.	
Amino-sulfonic acids . . . . .	379		
9-18. Other nitrogen compounds	380-400a		
19-38. Organometallic compounds	401-449		

*Note 1.* In order to facilitate cross referencing within the various parts of the comprehensive classification, the entire subject matter has been divided into a total of 4877 arbitrary units called "system numbers." Use of these numbers permits convenient reference to any other part of the systematic arrangement without respect to the particular volume in which this may occur. Such a device was necessary in the compiling of the work since the size of the final printed volumes, and hence the location of any given part could not be predicted in advance. A complete list of these "system numbers" has been published by the German Chemical Society in its *Leitfaden für die Benutzung von Beilstein's Handbuch*, 1929. Since every printed volume of the handbook indicates its system number scope on the binding, and in addition gives the appropriate system number at the top of every page, all desired cross references within the existing volumes can readily be effected without further supplementary aid.

*Note 2.* It should particularly be noted that in the Fourth Edition itself, the chemical literature is covered up to January 1, 1910, in each and every volume. In the First Series of supplementary volumes the literature covered is that published between 1910 and 1920.

## CHART 4 (Continued)

	System Numbers	Main Series	First Supple- mentary Series
<b>DIVISION II: ISOCYCLIC</b>			
1. Hydrocarbons . . . . .	450- 498	Vol. V 1922, 796 pp.	Vol. V 1930, 417 pp.
2. Hydroxy compounds . . . . .	499- 608	Vol. VI 1923, 1285 pp.	Vol. VI 1931, 642 pp.
3. Carbonyl compounds . . . . .	609	Vol. VII 1925, 955 pp.	Vol. VII-VIII 1931, 820 pp.
Mono and polycarbonyl compounds . . . . .	610- 736		
Hydroxy-carbonyl compounds . . . . .	737- 890	Vol. VIII 1925, 616 pp.	
4. Carboxylic acids . . . . .	891	Vol. IX 1926, 1063 pp.	Vol. IX 1932, 476 pp.
Mono and polycarboxylic acids . . . . .	892-1050		
Hydroxy-carboxylic acids . . . . .	1051-1281	Vol. X 1927, 1124 pp.	Vol. X 1932, 571 pp.
Carbonyl-carboxylic acids . . . . .	1282-1394		
Hydroxy-carbonyl- carboxylic acids . . . . .	1395-1504		
5. Sulfinic acids . . . . .	1505-1513	Vol. XI 1928, 443 pp.	Vol. XI-XII 1933, 608 pp.
6. Sulfonic acids . . . . .	1514		
Mono and polysulfonic acids . . . . .	1515-1544		
Hydroxy-sulfonic acids . . . . .	1545-1570		
Carbonyl-sulfonic acids . . . . .	1571-1574		
Hydroxy-carbonyl- sulfonic acids . . . . .	1575-1582		
Sulfonic-carboxylic acids, etc. . . . .	1583-1591		
7. Seleninic, selenonic acids, etc.	1591a		
8. Tellurinic, telluronic acids, etc.			
9. Amines . . . . .	1592	Vol. XII 1929, 1436 pp.	
Monoamines . . . . .	1593-1739		
Polyamines . . . . .	1740-1820	Vol. XIII 1930, 903 pp.	
Hydroxy-amines . . . . .	1821-1871		
Carbonyl-amines . . . . .	1872-1881	Vol. XIV 1931, 937 pp.	Vol. XIII-XIV 1933, 839 pp.
Amino-carboxylic acids . . . . .	1882-1920		
Amino-sulfinic acids . . . . .	1921		
Amino-sulfonic acids . . . . .	1922-1928		
10. Hydroxylamines . . . . .	1929-1939	Vol. XV 1932, 724 pp.	
11. Hydrazines . . . . .	1940-2084		
12. Azo compounds . . . . .	2085-2188	Vol. XVI 1933, 1040 pp.	Vol. XV-XVI 1934, 649 pp.
13. Diazo compounds . . . . .	2189-2204		
14-23. Other nitrogen compounds	2205-2251		
24-37. Organometallic compounds . . . . .	2252-2358		

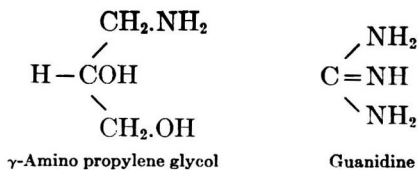
## CHART 4 (Continued)

	System Numbers	Main Series	First Supple- mentary Series	
<b>DIVISION III: HETEROCYCLIC</b>				
<b>Compounds with 1 cyclic OXYGEN</b>				
(or S, or Se, or Te) atom . . .	2360			
1. Stem nuclei . . . . .	2361-2377	Vol. XVII 1933, 617 pp.	Vol. XVII- XVIII-XIX 1934, 901 pp.	
2. Hydroxy compounds . . . . .	2378-2456			
3. Carbonyl compounds . . . . .	2457			
Monocarbonyl compounds	2458-2473			
Polycarbonyl compounds	2474-2503			
Hydroxy-carbonyl compounds . . . . .	2504-2569			
4. Carboxylic acids . . . . .	2570-2626	Vol. XVIII 1934, 701 pp.		
5-15. Sulfinic acids — organometallic compounds . . . . .	2627-2665			
<b>Compounds with 2 (or more) cyclic</b>				
<b>OXYGEN (or S, or Se, or Te)</b>				
atoms . . . . .	2666			
1. Stem nuclei . . . . .	2667-3031	Vol. XIX 1934, 500 pp.		
etc., etc.				
<b>Compounds with 1 cyclic</b>				
<b>NITROGEN atom . . . . .</b>				
	3032	Vol. XX 1935, 566 pp.		
1. Stem nuclei . . . . .	3033-3102			
2. Hydroxy compounds . . . . .	3103-3176	Vol. XXI 1935, 677 pp.	Vol. XX- XXI-XXII 1935, 756 pp.	
3. Carbonyl compounds . . . . .	3177-3241			
4. Carboxylic acids . . . . .	3242-3375			
5-14. Sulfinic acids — C-Mg compounds . . . . .	3376-3457	Vol. XXII 1935, 634 pp.		
<b>Compounds with 2 cyclic</b>				
<b>NITROGEN atoms . . . . .</b>				
	3458	Vol. XXIII 1936, 593 pp.		
1. Stem nuclei . . . . .	3459-3501			
2. Hydroxy compounds . . . . .	3502-3554	Vol. XXIV 1936, 577 pp.	Vol. XXIII- XXIV-XXV 1936, 825 pp.	
3. Carbonyl compounds . . . . .	3555-3633			
Hydroxy-carbonyl compounds . . . . .	3634-3638			
4. Carboxylic acids . . . . .	3639-3705	Vol. XXV 1936, 622 pp.		
5-18. Sulfonic acids — C-Hg compounds . . . . .	3706-3793			
<b>Compounds with 3-8 cyclic</b>				
<b>NITROGEN atoms . . . . .</b>				
	3794-4187	Vol. XXVI 1937, 656 pp.	Vol. XXVI- XXVII 1938	
<b>Compounds with both cyclic</b>				
<b>O + N atoms . . . . .</b>				
	4188-4720	Vol. XXVII 1937, 700 pp.		

the above rule no longer is applicable; thus  $\text{Br.C}_6\text{H}_4.\text{CHO}$  is a substitution product of benzaldehyde,  $\text{C}_6\text{H}_5.\text{CHO}$ , Division II (Isocyclic), Class 3 (Carbonyl compounds), and is therefore listed after all the functional derivatives of the latter have been taken up.

**Two or more functioning groups are present.** (a) *These functioning groups are alike.* When the like functional groups are attached to different carbons the substance may be classed by inspection with the polyfunctional derivatives of the corresponding class: thus  $\text{HO.CH}_2.\text{CH}_2.\text{OH}$  is evidently a member of Division I (Acyclic), Class 2 (Hydroxy compounds). In cases where the functioning groups are on the same carbon, however, it will be observed that Rule 1 (page 8) will again apply: thus,  $\text{CH}_3.\text{CH}(\text{SO}_3\text{H})_2$  is listed as a derivative of acetaldehyde,  $\text{CH}_3.\text{CHO}$ , Division I (Acyclic) Class 3 (Carbonyl compounds).

(b) *These functioning groups are different.* If these unlike functioning groups are located on different carbon atoms the compound will be listed under the latest class systematically represented, the particular subclass being determined by the nature of the several functional groups. Thus,  $\gamma$ -amino propylene glycol is listed in Division I (Acyclic), Class 8 (Amines), Subclass D, (Hydroxy-amines), Rubric 2, (Amino derivatives of dihydroxy compounds). If, however, the several unlike functioning groups are attached to a single carbon atom Rule 1 (page 8) again must be invoked.



Thus, guanidine is regarded as a coupling product of  $\text{CO}(\text{OH})_2$  and  $\text{NH}_3$ , and is therefore listed under carbonic acid in Division I (Acyclic), Class 4 (Carboxylic acids), Subclass L (Hydroxy-carboxylic acids).

The determination of the division, class and sometimes the subclass of the compound in this way definitely determines the volume of Beilstein to be consulted. Very often with this much data alone the approximate location of the substance can be ascertained by rapid survey of the table of contents in the front of the volume. When desired, however, further subclassification can be effected by calculation of the empirical formula. Thus,  $\text{C}_6\text{H}_5.\text{CO}.\text{CH}_2.\text{C}_6\text{H}_5$



evidently is located in Division II (Isocyclic), Class 3 (Carbonyl compounds), Subclass A (Monocarbonyl compounds). Its empirical composition  $C_{14}H_{12}O$  corresponds to the expression  $C_nH_{2n-16}O$  and hence by examination of succeeding rubrics we find this group of 14 carbon isomers included in Rubric 8. By turning to the appropriate pages for this group we readily locate the desired individual compound with facility.

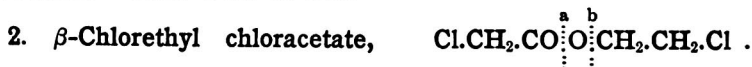
## (2) THE SUBSTANCE IS ITSELF A FUNCTIONAL DERIVATIVE

When the substance to be located is a functional derivative it will contain one or more linkages of carbon to some other "inorganic" element. By applying a process of hydrolytic splitting which is the exact reverse of "anhydrosynthesis" a number of smaller cleavage products can be obtained. In this cleavage process rupture of a single linkage is followed by addition of OH to the carbon atom and H to the inorganic atom; in case the inorganic group is doubly bound to carbon, cleavage is followed by addition of O to the carbon and  $H_2$  to the inorganic atom. When all of the cleavage products thus derived are themselves index compounds the next step involves merely the determination of which one comes latest in the systematic arrangement, the desired compound being listed thereunder as a functional derivative in an order depending upon the nature and number of the coupling products. When some of the primary cleavage products are themselves functional derivatives, however, the process must be repeated with these until ultimately only index compounds and coupling compounds result. In determining the location of given substances in this way care must be taken to comply with all of the requirements for the formation of functional derivatives given in Chart 3.

**Examples of procedure.** The general procedure employed will best be evident by considering some actual examples.

1. Ethyl acetate,  $CH_3.CO\overset{a}{\underset{\vdots}{\underset{\vdots}{O}}}\overset{b}{\underset{\vdots}{\underset{\vdots}{O}}}:CH_2.CH_3$ . There are two different points of union of a carbon atom with an inorganic atom, viz., at (a) and at (b). In this particular case the same cleavage products result whether splitting occurs at (a) or at (b). They are acetic acid,  $CH_3.CO.OH$ , and ethyl alcohol,  $CH_3.CH_2.OH$ . Since both of these are acyclic compounds the original ethyl acetate is listed in Division I (Acyclic). Since acetic acid is a member of Class 4 (Carboxylic acids) it occurs later in the system

than ethyl alcohol Class 2 (Hydroxy compounds), and the substance ethyl acetate is therefore listed as a functional derivative of acetic acid with ethyl alcohol as the coupling compound. It will therefore be listed after the data on acetic acid itself have been discussed.<sup>1</sup> *Ans.* Beil. II-125.



Since non-functioning substituents always follow functional derivatives the substituents are not subjected to the process of hydrolytic splitting in determining the fundamental index compounds. This simplifies this example to a complete analogy to the case of ethyl acetate just discussed. Thus the cleavage products from either (a) or (b) are chloracetic acid,  $\text{Cl} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{OH}$ , and  $\beta$ -chlorethyl alcohol,  $\text{ClCH}_2 \cdot \text{CH}_2 \cdot \text{OH}$ . Of these, chloracetic acid comes latest in the system and the compound is therefore listed as a functional derivative of chloracetic acid with  $\beta$ -chlorethyl alcohol. Note that the substance is not listed as a substitution product of ethyl acetate. *Ans.* Beil. II-198.



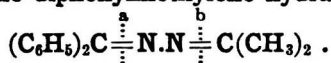
Here there are also two places at which carbon is connected to an inorganic element but the cleavage products at the two bonds are different. Thus, at (a) the splitting products are  $\text{CH}_3 \cdot \text{OH}$  and  $\text{CH}_3 \cdot \text{O} \cdot \text{NH}_2$ ; at (b) they are  $\text{CH}_3 \cdot \text{NH} \cdot \text{OH}$  and  $\text{CH}_3 \cdot \text{CH}$ . Of these four molecules the second,  $\text{CH}_3 \cdot \text{O} \cdot \text{NH}_2$ , must evidently be split again since  $-\text{O} \cdot \text{NH}_2$  is not in the list of functioning classes (pages 10-11). The products of this subsidiary cleavage are  $\text{CH}_3 \cdot \text{OH}$  and  $\text{NH}_2 \cdot \text{OH}$ . The original substance has now been reduced to the fragments  $\text{CH}_3 \cdot \text{OH}$ ,  $\text{CH}_3 \cdot \text{NH} \cdot \text{OH}$ , and  $\text{NH}_2 \cdot \text{OH}$ . Both of the two organic materials upon which classification must depend are acyclic substances, throwing the matter entirely into Division I. The latest of the two to be listed must be  $\text{CH}_3 \cdot \text{NH} \cdot \text{OH}$  (methyl hydroxylamine) since Class 9 (Hydroxylamines) follows Class 2 (Hydroxyl compounds). The original material will therefore be found in Division I, Class 9, under methylhydroxylamine as its functional derivative with methyl alcohol. *Ans.* Beil. IV-534.

<sup>1</sup>A concise method of expressing the volume and page number for the location of individual compounds in the main and supplementary series of the Fourth Edition will be followed in this book; e.g., Beil. III-125. A reference to a volume of the first supplementary series would then become of the form Beil. XXII<sub>1</sub>-373; or for a second supplementary series, Beil. XVI<sub>2</sub>-214.

4. Benzaldoxime,  $C_6H_5.CH \overset{a}{\underset{\vdots}{\parallel}} N.OH$ . The cleavage products at the double bond (*a*) are benzaldehyde,  $C_6H_5.CHO$ , and hydroxylamine,  $NH_2.OH$ . Since only the first is organic, the desired oxime is evidently a functional derivative of the isocyclic benzaldehyde. The latter is evidently in Division II (Isocyclic), Class 3 (Carbonyl compounds). Furthermore its formula shows that it is a monocarbonyl compound, which of course is included in Subclass A. These data suffice to locate the material in Volume VII. Since the empirical formula of benzaldehyde is  $C_7H_6O$  its general empirical composition is represented by  $C_nH_{2n-8}O$ . This group is found to constitute Rubric 4 of the indicated subclass, and the individual substance  $C_7H_6O$  is found as the first representative within the limits of this classification. The original oxime is then discovered in the list as a functional derivative of benzaldehyde with the inorganic coupling compound hydroxylamine,  $NH_2.OH$ . *Ans.* Beil. VII-218.

In passing it may be noted that since all oximes will be formed as functional derivatives of the carbonyl compound with the inorganic coupling compound  $NH_2.OH$ , they will invariably be listed as derivatives of the parent carbonyl compound. Contrast this with hydrazones in examples 6 and 7.

5. Isopropylidene-diphenylmethylene-hydrazine,



Hydrolytic cleavage at (*a*) yields benzophenone,  $(C_6H_5)_2CO$ , and  $(CH_3)_2C = N.NH_2$  of which the latter can be further split at the bond (*b*) yielding in turn acetone,  $(CH_3)_2CO$ , and hydrazine,  $NH_2.NH_2$ . Inspection of the two organic products classifies the original substance with Division II (Isocyclic), Class 3 (Carbonyl compounds). Pursuing the position of benzophenone by its monocarbonyl character, and by its general and particular empirical composition as in the preceding illustration, we find the indicated example to be a second degree functional derivative of benzophenone, first by coupling with the inorganic coupling compound hydrazine, and second by coupling of this with acetone. *Ans.* Beil. VII-417.

6. Benzaldehyde methylhydrazone,  $C_6H_5.CH \overset{a}{\underset{\vdots}{\parallel}} N.NH \overset{b}{\underset{\vdots}{\parallel}} CH_3$ . Cleavage of this material in a way completely analogous to that in example 5 shows that the substance is in Division II (Isocyclic), Class 3 (Carbonyl compounds) as a second degree functional derivative of benzaldehyde. *Ans.* Beil. VII-225.

7. **Benzophenone phenylhydrazone**,  $(\text{C}_6\text{H}_5)_2\text{C} \overset{\text{a}}{\underset{\cdot\cdot\cdot}{\parallel}} \text{N} \overset{\text{b}}{\underset{\cdot\cdot\cdot}{\parallel}} \text{C}_6\text{H}_5$ .  
 Cleavage at (a) yields benzophenone,  $(\text{C}_6\text{H}_5)_2\text{CO}$ , and phenyl hydrazine,  $\text{C}_6\text{H}_5\text{NH.NH}_2$ ; cleavage at (b) gives phenol,  $\text{C}_6\text{H}_5\text{OH}$  and a compound  $(\text{C}_6\text{H}_5)_2\text{C} = \text{N.NH}_2$ . Since the latter is not a true hydrazine derivative of the type  $\text{R.NH.NH}_2$  it must be further split in the usual way into benzophenone and hydrazine. Of the four different ultimate cleavage products which thus finally result, the latest in the systematic arrangement is phenylhydrazine (Division II, Class 10). The original phenylhydrazone is therefore listed as a functional derivative of phenylhydrazine with the organic coupling compound benzophenone. *Ans.* Beil. XV-148.


Note particularly in this illustration that the substance phenylhydrazine is not further split by a reverse anhydrosynthesis because to do so would violate a general rule which requires that *index compounds* obtained by a cleavage process shall not be further simplified. Note furthermore that hydrazones are listed either under the parent carbonyl compound or under the corresponding hydrazine according to which occurs latest in the system. This is in marked contrast to the procedure which results with oximes (Example 4).

8. **N-Ethyl-p-phenylenediamine**,  $\text{NH}_2\text{.C}_6\text{H}_4 \overset{\text{a}}{\underset{\cdot\cdot\cdot}{\parallel}} \text{NH} \overset{\text{b}}{\underset{\cdot\cdot\cdot}{\parallel}} \text{CH}_2\text{.CH}_3$ .  
 Cleavage at (a) yields p-aminophenol,  $\text{NH}_2\text{.C}_6\text{H}_4\text{OH}$ , and ethyl amine,  $\text{CH}_3\text{.CH}_2\text{.NH}_2$ ; neither of these substances are further split because they are index compounds in their own right. Cleavage at (b), however, gives p-phenylenediamine,  $\text{NH}_2\text{.C}_6\text{H}_4\text{.NH}_2$ , and ethyl alcohol,  $\text{CH}_3\text{.CH}_2\text{.OH}$ . Despite the fact that of these four cleavage products the latest in the system is p-aminophenol, to list the original herewith would require violation of the rule that in the process of anhydrosynthesis the OH must split from a carbon atom of the coupling compound and not the index compound. Consequently the material is regarded as a functional derivative of p-phenylenediamine with ethyl alcohol as coupling compound. It will therefore be listed in Division II (Isocyclic), Class 8 (Amines), Subclass B (Diamines). *Ans.* Beil. XIII-75.

9. **m-Nitrobenzene N-methylsulfonamide**,  $\text{NO}_2\text{.C}_6\text{H}_4\text{.SO}_2 \overset{\text{b}}{\underset{\cdot\cdot\cdot}{\parallel}} \text{NH} \overset{\text{a}}{\underset{\cdot\cdot\cdot}{\parallel}} \text{CH}_3$ .  
 Cleavage of the carbon-nitrogen linkage at (a) yields the products m-nitrobenzenesulfonamide,  $\text{NO}_2\text{.C}_6\text{H}_4\text{.SO}_2\text{.NH}_2$ , and methyl

alcohol,  $\text{CH}_3\text{OH}$ . The first of these is evidently a functional derivative itself and must be further split into *m*-nitrobenzenesulfonic acid,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$ , and ammonia,  $\text{NH}_3$ . Since the nitro group is a non-functioning substituent and since the sulfonic acid group is one of the 28 class functions, further cleavage is not permissible. On the other hand, cleavage of the original molecule at (b) yields *m*-nitrobenzenesulfonic acid as before, together with methyl amine,  $\text{CH}_3\cdot\text{NH}_2$ . Since an attempted anhydrosynthesis between this pair of substances would not involve the splitting out of a hydroxyl attached to a carbon atom of the coupling compound, however, the original substance must be construed as a second degree derivative involving, first, the combination of the index compound *m*-nitrobenzenesulfonic acid with the inorganic coupling compound ammonia, and second, the second degree coupling of this with methyl alcohol.

The index compound, *m*-nitrobenzenesulfonic acid, is itself evidently a substitution product of benzenesulfonic acid and will therefore be listed in Division II (Isocyclic), Class 6 (Sulfonic acids) accompanied by its derivatives. *Ans.* Beil. XI-70.

10. Methyl 2-ethoxybenzoate,   $\text{CO}\cdot\text{OCH}_3$   
 $\text{OC}_2\text{H}_5$ . Inspection of

this molecule indicates that its cleavage products are *o*-hydroxybenzoic acid, methyl alcohol, and ethyl alcohol. The material is therefore indexed as a derivative of *o*-hydroxybenzoic acid in Division II (Isocyclic), Class 4 (Carboxylic acids), Subclass J (Hydroxycarboxylic acids). This fixes the Beilstein volume as X, and the individual salicylic acid is readily located. The desired compound is evidently a functional derivative involving alteration of both of the two different functional groups which are present. According to rule (page 24) we follow along the various organic and inorganic functional derivatives of the hydroxyl (the earliest of the two groups) group to the point where alteration of the carboxyl is begun. Each first degree alteration of this group is combined with all possible alterations of the hydroxyl before another first degree function is listed. Thus directly under methyl salicylate  $\text{CH}_3\cdot\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$  we find the corresponding methyl ether,  $\text{CH}_3\cdot\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OCH}_3$ , and immediately following this the desired ethyl ether,  $\text{CH}_3\cdot\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OC}_2\text{H}_5$ . *Ans.* Beil. X-72.



## CHAPTER VII

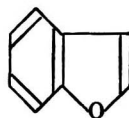
### PROBLEMS IN THE USE OF BELSTEIN'S "HANDBUCH"

**PROBLEM A.** Object: Designed to train in finding simple index compounds.

After systematically locating the data on each of the following compounds express the volume and page in the usual way (e.g., X-750) and give the "trivial" name for each substance.

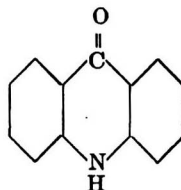
1. 2, 5-Dimethylhexadiene-2, 4
2.  $\alpha, \beta, \gamma, \delta$ -Tetrahydroxybutane

23.



3. Butanol-3-one-2
4. 2-Methylbutene-2-acid-1

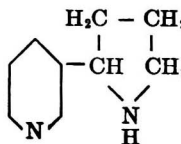
24.



5. Hexadiene-2, 4-di-acid-1, 6
6. Propanol-3-acid-1
7. 1, 5-Diaminopentane
8. 1, 2, 4, 5-Tetramethylbenzene

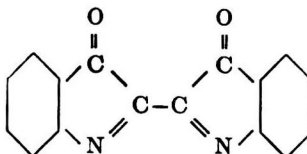
9. Hexahydroxycyclohexane
10. p-Isopropylbenzaldehyde
11. 3, 4-Dihydroxybenzaldehyde
12. Biphenyl-o, o'-dicarboxylic acid

25.



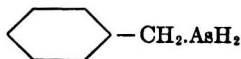
13. 3, 4-Dihydroxybenzene-dicarboxylic acid-1, 2
14. 1-Hydroxynaphthalenesulfonic acid-4

26.



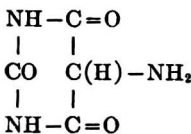
15. 1, 2, 4-Trimethyl-5-aminobenzene
16. 2, 4'-Diaminobiphenyl

27.



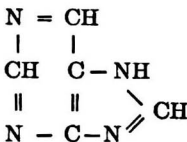
17. p-Tolyldiazine
18. Resorcinolphthalein

28.



19. Furan- $\alpha$ -carboxylic acid
20. 2-Methylquinoline
21. Aniline-p-sulfonic acid
22. 2-Phenylquinoline-carboxylic acid-4

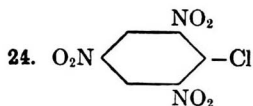
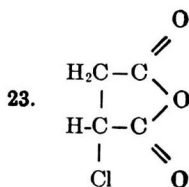
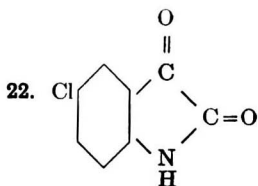
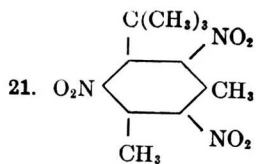
29.



42 PROBLEMS IN THE USE OF BELLSTEIN'S "HANDBUCH"

**PROBLEM B. Object:** To test knowledge of rules on Pages 8 and 9 and to test ability to locate simple substitution products.

1.  $\text{Br} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$
2.  $\text{Br} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{SO}_3\text{H}$
3.  $\text{CH}_3 \cdot \text{CHCl} \cdot \text{SO}_3\text{H}$
4.  $\text{CH}_2 \cdot \text{C}(\text{Br}) \cdot \text{SO}_3\text{H}$
5.  $\text{Cl} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{Cl}$
6.  $\text{C}_6\text{H}_5 \cdot \text{C}(\text{Cl}) \cdot \text{C}(\text{Cl}) \cdot \text{C}_6\text{H}_5$
7.  $\text{NH}_2 \cdot \text{C}(\text{:NH}) \cdot \text{NH}_2$
8.  $p\text{-NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{Cl}$
9.  $4\text{-Br} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{Br}$
10.  $\text{C}_6\text{H}_5 \cdot \text{C} \cdot \text{Cl}_3$
11.  $p\text{-NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{NH}_2$
12.  $\text{HCN}$
13.  $\text{Br} \cdot \text{CN}$
14.  $\text{CH}_3 \cdot \text{C}(\text{:NH}) \cdot \text{NH}_2$
15.  $\text{COCl}_2$
16.  $\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{NO}_2$
17.  $\text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{NOH}$
18.  $\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{Cl}$
19.  $\text{CHI}_3$
20. 5-Bromo-2,4,6-triiodo-1,3-dinitrobenzene





**PROBLEM C. Object: To test ability to locate simple functional derivatives.**  
(See Note.)

- |   |   |
|---|---|
| 1. Pentandioxime-1, 4   | 17. Benzenesulfonanilide                          |
| 2. Trimethyl $\alpha$ , $\beta$ , $\gamma$ -propanetricarboxylate | 18. Benzenesulfon-p-toluidide                     |
| 3. Acetoacetamide   | 19. 5-Nitrofuroanilide                            |
| 4. Acetaldehyde semicarbazone                                     | 20. p-Acetylamino-dimethylaniline                 |
| 5. N, N'-Diacetyltetramethylenediamine                            | 21. o-Sulfobenzoic anhydride                      |
| 6. N-Acetyl-N-methylhydrazine                                     | 22. Piperildioxime                                |
| 7. Isophthalaldehyde tetracetate                                  | 23. Hydrocinnamaldehyde<br>p-nitrophenylhydrazone |
| 8. Camphor phenylhydrazine  | 24. 4, 4'-Diaminobiphenyl-2, 2'-disulfonamide     |
| 9. 2-Acetoxyanthraquinone   | 25. Isonitrosopropiophenone                       |
| 10. 1, 5-Dihydroxyanthraquinone di- $\beta$ -naphthyl ether       | 26. Benzenesulfonyl-1-tryptophane                 |
| 11. Camphoroxime benzoate   | 27. Ethyl ( $\alpha$ -formyl) phenylacetate       |
| 12. 4-Methoxybenzamide  | 28. Dichloroacetaldehyde ethyl phenyl acetal      |
| 13. N-Benzoylbenzylamine  | 29. N-(p-benzyoxyphenyl) phthalimide              |
| 14. Benzophenone anil   | 30. 4-Benzeneazo-1-phenyl-3-methylpyrazolone-5    |
| 15. N-Methylantranilamide   |   |
| 16. p-Acetylaminoazobenzene                                       |   |

*Note:* Always remember that many substances first prepared since 1910 (and therefore not listed in the main series) will be listed in corresponding supplementary volumes.

**PROBLEM D. Further practice in locating functional derivatives. (cf. Note to Prob. C.)**

- |  |  |
|--|--|
| 1. Ethyl oxamidate                                 | 11. Benzenesulfonyl-N-methyl-aniline     |
| 2. Hydroquinone-O, O'-diacetic acid                | 12. N-Benzenesulfonyl-N'-phenylhydrazine |
| 3. Hexa-acetoxybenzene                             | 13. N-Phenacylaniline                    |
| 4. Diethyl 4-nitrocinnamal-malonate                | 14. Fural-p-toluidine                    |
| 5. 3, 6-Dimethoxyphthalonitrile                    | 15. Phenacyl N-phenacylanthra-nilate     |
| 6. Camphoroxime $\beta$ -sulfonic acid             | 16. Methyl orange                        |
| 7. N-( $\beta$ -phenoxyethyl)-p-toluenesulfonamide | 17. 3-Acetoxymercuri-4-hydroxyazobenzene |
| 8. 1, 3, 5-Triacetylaminobenzene                   | 18. S-Methyl isothiourrea                |
| 9. p-(N-benzamino) phenol                          | 19. 4-Anilinonaphthoquinone-1, 2         |
| 10. p-Aminophenyl benzoate                         | 20. 2-Anilinonaphthoquinone-1, 4         |

**PROBLEM E. Miscellaneous.**

- |   |                                   |
|---|-----------------------------------|
| 1. Mellitic anhydride                                 | 11. Methyl n-propyl nitrosoamine  |
| 2. Tetramethylene-1, 4-disulfone                      | 12. Diphenylcarbanyl chloride     |
| 3. Phenylhydrazine-p-sulfonic acid                    | 13. Thiophene                     |
| 4. 1-Phenyl-3-methyl-pyrazolone-5                     | 14. Thiodiglycol                  |
| 5. Trional  | 15. Pyruvic p-anisidide           |
| 6. The double diazonium hydro-chloride from benzidine | 16. Tribenzoylmethane             |
| 7. Indanthrone  | 17. Thioindigo                    |
| 8. $\alpha$ , $\beta$ -Dichlorodiethyl ether          | 18. Indigo-5, 5'-disulfonic acid  |
| 9. Ethyl thiocyanate                                  | 19. N, N', N''-Triphenylguanidine |
| 10. Ethyl isothiocyanate                              | 20. Mercuric acetylde             |
|   | 21. Tetraethyl lead               |
|   | 22. Cyanidine hydrochloride.      |

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**Author** HUNTRESS .....

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BELLSTEIN'S HANDBUCH DE ORGANISCHEN CHEMIE

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A brief introduction to