Abbreviation	German	English
A.	Äthanol	ethanol
Acn.	Aceton	acetone
Ae.	Diäthyläther	diethylether
alkal.	alkalisch	alkaline
Anm.	Anmerkung	footnote
B.	Bildungsweise(n), Bildung	formation
Bd.	Band	volume
Bzl.	Benzol	benzene
Bzn.	Benzin	petroleum ether
bzw.	beziehungsweise	or, respectively
D	Dichte	density
Diss.	Dissertation	dissertation, thesis
E	Ergänzungswerk des Beilstein-Handbuchs	Beilstein supplement
E	Erstarrungspunkt	freezing point
E.	Äthylacetat	ethyl acetate
Eg.	Essigsäure (Eisessig)	acetic acid
engl. Ausg.	englische Ausgabe	english edition
F	Schmelzpunkt	melting point
Gew.-%	Gewichtsprozent	percent by weight
H	Hauptwerk des Beilstein-Handbuchs	Beilstein main work
h	Stunde(n)	hour(s)
konz.	konzentriert	concentrated
korr.	korrigiert	corrected
Kp	Siedepunkt	boiling point
Me.	Methanol	methanol
min	Minute	minute
n	Brechungsindex	refractive index
opt.-inakt.	optisch inaktiv	optically inactive
PAe.	Petroläther	petroleum ether
Py.	Pyridin	pyridine
RRI	Ring Index (2. Aufl. 1960)	The Ring Index (2nd. ed. 1960)
RIS	Ring Index (2. Aufl. 1960), Ergänzung	The Ring Index (2nd. ed. 1960), Supplement
S.	Seite	page
s	Sekunde	second
s.	siehe	see
s. a.	siehe auch	see also
s. o.	siehe oben	see above
sog.	sogenannt	so called
Spl.	Supplement	supplement
... stdg. (z.B. 3-stdg.)	... stündig (z.B. 3-stündig)	for ... hours (e.g. for 3 hours)
s. u.	siehe unten	see below
Syst. Nr.	System-Nummer	system number
Tl.	Teil	part
unkorr.	unkorrigiert	uncorrected
unverd.	unverdünnt	undiluted
verd.	verdünnt	diluted
vgl.	vergleiche	compare (cf.)
W.	Wasser	water
wss.	wäßrig	aqueous
z.B.	zum Beispiel	for example (e.g.)
Zers.	Zersetzung	decomposition

How to use Beilstein

Beilstein Handbook
of Organic Chemistry

Beilstein Institute
Frankfurt/Main

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EV 1960-79

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1 Questions about Beilstein

"Do you know Beilstein?" Even readers whose answer is yes will learn things worth knowing and useful about Beilstein in this informative booklet.

1.1 What is Beilstein?

„Beilstein", – is the short name, familiar to all chemists, for *the* handbook of carbon compounds: *Beilsteins Handbuch der Organischen Chemie.* This work has been an indispensable aid for almost a century for every chemist working in the field of organic chemistry.

In the 4th edition of *"Beilsteins Handbuch der Organischen Chemie"*, which has been in print since 1918, the data published over set periods in the scientific literature on the preparation and properties of all carbon compounds has been compiled. The complete work consists of 5 series (Basic Series and 4 Supplementary Series) covering the periods listed in Table 1.

Preparations are currently in progress for the Fifth Supplementary Series (E V).

Table 1: The Series of the Beilstein Handbook (4th edition)

Series	Abbreviation	Period of literature completely covered	Colour of label on spine
Basic Series	H	up to 1909	green
Supplementary Series I	E I	1910–1919	red
Supplementary Series II	E II	1920–1929	white
Supplementary Series III	E III	1930–1949	blue
Supplementary Series III/IV	E III/IV*)	1930–1959	blue/black
Supplementary Series IV	E IV	1950–1959	black

*) Volumes 17–27 of Supplementary Series III and IV, covering the heterocyclic compounds are combined in a joint issue.

Each of these series comprises 27 volumes (or groups of volumes) in which the individual compounds are arranged according to the *Beilstein System.* Which compounds are dealt with in which Beilstein volumes is shown in Table 3 (p. 16) and Table 4 (p. 19).

Beilstein is unique among handbooks of organic chemistry in that it provides a collection of critically examined and exactly reproduced data on the known carbon compounds. It is in this respect superior to all other straight bibliographical documentation and series of abstracts.

1.2 How is Beilstein Compiled?

In the Beilstein Institute in Frankfurt/Main, more than 100 chemists and physicists are engaged in careful study of all the relevant primary literature, after which millions of literature abstracts are prepared and ordered according to the Beilstein System–to be discussed later. This material is subsequently critically reviewed. By checking the data from the various literature sources for internal consistency, obvious errors and contradictions in the primary literature can be eliminated as far as possible or tagged with an appropriate comment. The manuscripts so prepared, which present a concentrate of the primary literature, free of incorrect and superfluous information, are finally re-edited several times to ensure that the printed Beilstein volumes are as free of errors as at all possible.

1.3 What does Beilstein Contain?

Beilstein covers all carbon compounds dealt with in the scientific literature which have been accurately described, obtained in a state of sufficient purity and whose constitution is known.

Their description covers the following aspects:

- **Constitution and Configuration**

  (With particular regard to clarification of these aspects, the most recent literature findings up to the date of publication of each subvolume are used).

- **Natural Occurrence and Isolation from Natural Products**

- **Preparation, Formation and Purification**

  (Biochemical methods of formation are included when these are suitable for use on a preparative scale).

- **Structural and Energy Parameters of the Molecule**

  (Including data on:
  conformation, conformer equilibrium, energy separation between conformers;
  bond lengths and angles;
  electron distribution;
  dipole moment;
  quadrupole moment;
  polarisability;
  coupling phenomena;
  molecular deformation;
  molecular potentials;
  dissociation energy;
  ionisation potential etc.).

- **Physical Properties**

  (Including data on:
  description of the physical state and mechanical properties;
  transport phenomena;
  energy data;
  optical properties;
  spectra;
  magnetic properties;
  electrochemical behaviour;
  physical properties of multicomponent systems etc.).

- **Chemical Properties**

  (In this section, reactions considered to be of sufficient importance are described for each compound with all types of reacting species).

- **Characterization and Analysis**

- **Salts and Addition Compounds**

In contrast to abstract services which merely name the topics treated in the literature references cited (often widely scattered), Beilstein contains tested specific information which often saves its users the labour of procuring and reading the primary literature. Furthermore, all data is checked with the greatest possible care for its soundness, internal consistency, newness and significance by competent scientists, in the light of modern chemical thinking. Clearly false information in the primary literature is corrected; data on preparations of insufficient purity, duplicated data and data on trivial findings are not taken into consideration. Much of the information cited is supplied with cross-references and critical comments. Statements of a speculative nature are checked against newer results drawn from later and the very latest sources, ensuring that the work is kept completely up to date.

Thus the Beilstein Handbook is not only an invaluable and indispensable work of reference for every scientist engaged in the field of organic chemistry but also helps the attentive user to avoid pitfalls and provides stimulation for further experiments.

Serving as sources of information for Beilstein are the international scientific journals as well as the patent literature, and, in selected cases important theses and conference reports. All factual data taken over in the text of the

handbook is furnished with precise details of its source. A *list of the full names of the journals and other publications made use of,* together with the abbreviations used for them is to be found at the beginning of each Beilstein volume. Tables of other abbreviations used in the handbook are also to be found here, together with, in the later volumes, explanations of the stereochemical nomenclature and a transliteration table for the cyrillic alphabet.

1.4 Who Needs Beilstein?

Without doubt the most frequent users of the Beilstein Handbook will be chemists in universities, industry and research institutes who are working in the field of organic chemistry and who are best able to assess its value as an indispensable aid in their daily research. As can be seen however from the list of subject groups dealt with in Beilstein (on p. 6 f.), the handbook may also prove of value to physicists, analysts, chemical engineers, biochemists, biologists and the medical profession for the solution of part of their problems, since it provides exactly checked data.

The Beilstein Handbook is the most extensive collection of physical data in printed form in the world!

1.5 How is the Complete Work Arranged?

The 4th edition of Beilstein, in print since 1918, is divided into series and volumes.

The series (H, E I, E II, . . .), are devoted to the literature of consecutive periods (cf. Table 1, p. 5). It must be emphasised once again that each series of Beilstein is considerably more up to date than would be indicated by the final date of complete literature coverage given in the table, since important new findings from the most recent literature are included up to the time of publication of each volume. This is especially the case where corrections to the constitution or configuration of a compound, on the basis of new research results, are involved.

Since the classification of the subject matter in each of the supplementary series is the same as that chosen for the 27 volumes of the Basic Series, any particular volume of each supplementary series always contains the same classes of compounds (and *only* these) as the volume of the Basic Series with the same number. This correlation of subject matter classification, of benefit to the user, necessitated a further subdivision of most volumes of E III and E IV which are several times more extensive than the Basic Series. Thus for example, vol. 1 of E III consists of 3 subvolumes and vol. 1 of E IV of 6 subvolumes. By contrast in E I, 2 or 3 nominal volumes are combined together into a single volume in several cases.

Further to the 27 volumes of text, vols. 28 and 29 contain a general subject index (index of compound names) and a general formula index (see p. 11 f.).

The additional volumes 30 and 31, published in 1938, which were reserved for particular groups of compounds, namely the naturally occurring polyisoprenes and the carbohydrates, have been discontinued. The polyisoprenes have been incorporated into vols. 1–27 according to their constitutional formula following the general rules of the Beilstein System since the time of publication of E III, the carbohydrates since the time of publication of E IV.

The classification of compounds into compound classes and the arrangement of the individual compounds within these classes is determined by the *Beilstein System.* The latter consists of a series of rules by means of which *every and any* carbon compound can be assigned *one* specific location within the overall array of all carbon compounds. The total array is subdivided by 4720 *system numbers* which can be used for the purpose of orientation within Beilstein.

A summary of the contents of the 27 volumes of the Beilstein Handbook is presented in Table 4, p. 19.

1.6 How are the Individual Beilstein Items Arranged?

First of all, the heading of each item contains the most important *names* in bold-face type, selected according to the principles mentioned in section 2.1.2 (p. 11 f.); further names in spaced type are considered by the editors as less suitable (usually on account of poor compatibility with official nomenclature rules). Following the *empirical formula* and the *constitutional formula* the headings may further contain a *back-reference.* A back-reference such as "H 93; E II 64; E III 190" in a volume of Supplementary Series IV means that previous items on this compound are to be found in the same volume of the Basic Series on p. 93, of Supplementary Series II on p. 64, and of Supplementary Series III on p. 190. The prefix "vgl." (engl. "cf.") which is sometimes encountered in front of the back-reference, indicates that in the earlier items the compound(s) prepared may have had a different configuration. The lack of a back-reference implies that the compound involved is described *for the first time* in the series concerned.

In this case it is often possible to locate *related* compounds, described in earlier Beilstein series with the aid of the *coordinating reference.* Such coordinating references are to be found along with the series number, volume number and system number at the top of each *odd-numbered* page of the handbook. The coordinating reference indicates the page of the Basic Series to which the item would have been assigned*).

*) In the coordinating reference of the volumes of E IV the corresponding pages of E III are given alongside those of the Basic Series.

The pages of different supplementary series with identical coordinating references thus contain items on compounds with the same or closely related constitutions.

At the top of the *even-numbered* pages of the handbook is the designation of the *compound class* to which the compounds dealt with on that page belong.

The text of the items is set out in standardised form according to content, the latter being sorted into main subject groups. A list of the main subject groups is to be found in section 1.3, p. 6 f. Within the main subject groups the subject matter is also arranged systematically, e.g. within the main group "Chemical Properties" are ordered the subgroups "Reactions Involving No Other Identifiable Species", "Reactions with Non-carbon Compounds" and "Reactions with Carbon Compounds". As previously mentioned, all data are accompanied by bibliographical details of the literature source from which they were taken.

Corrections and additions, which where necessary are appended at the end of the relevant Beilstein volume, are integrated in the following supplementary series and are thus only of significance until such times as the latter is published.

2 How to Search for and Find Compounds in Beilstein

The *Table of Contents* at the beginning of each subvolume can only give a broad outline of the handbook's layout. For locating *individual* compounds more selective means are required; two alternative methods are available:

1. Use of the *indexes* (formula and subject indexes),
2. Use of the *Rules of the Beilstein System* (for direct searching in the text of the Beilstein volumes).

The second approach offers the advantage of being independent of other requirements such as a knowledge of chemical nomenclature and index practice. Without doubt however, familiarity with the entire Beilstein System is not to be acquired without some effort. In section 2.2 of this guide an attempt is made none the less, to provide the user with a considerably shortened and simplified version of the principles of the Beilstein System, which should enable him to determine which volume is relevant for a particular compound by means of a straight-forward schematic approach.

Independently of the above, searching with the help of the indexes can be recommended, in particular to those users with some experience of nomenclature. *Complete General Indexes* are of course only available for those series which have been concluded.

2.1 Searching with the Help of the Indexes

A *subject index* (name index of the compounds dealt with) is included at the end of each Beilstein volume (subvolume); all volumes from E III onwards further contain a *formula index* (index of empirical formulae). In addition there also exist cumulative indexes:

General Subject Index (vol. 28, 2 subvolumes) and
General Formula Index (vol. 29, 3 subvolumes).

The editions of these indexes published in 1955–1957 cover the entire contents of the first three handbook series (Basic Series, E I and E II). Collective indexes of smaller compass (collective subject and formula indexes) exist for a few volumes of E III. A synopsis is to be found in Table 2.

Table 2: Collective Subject Indexes and Collective Formula Indexes for Parts of Supplementary Series III (E III)

Collective subject indexes and collective formula indexes for volume number:	located in subvolume:
5	5/4
6	6/9
7 and 8	8/5 and 8/6
9 and 10	10/6 and 10/7
12 to 14	14/4 and 14/5

In E IV *cumulative subject indexes* and *cumulative formula indexes* are provided for individual volumes (e.g. vol. 1) or groups of volumes (e.g. vols. 17 and 18). These are indexes which cover the contents of all series of the volume(s) in question (Basic Series to E IV). In these cumulative registers the compound names conform to the latest nomenclature.

2.1.1 The Formula Indexes

In the formula indexes of Beilstein compounds are listed according to their empirical formula, in each case with *one* name. Standard prefixes and symbols (e.g. *R*, *cis*) are not included, with the result that stereoisomers whose names only differ by such a prefix are combined in a *single* index entry.

2.1.2 The Subject Indexes (Compound Name Indexes)

Use of the formula index is usually the surest and quickest method of searching for an individual compound. For searches of wider scope however, e.g. for a compound plus its derivatives, the subject index (compound name index) is better suited but requires an adequate knowledge of nomenclature.

With a view to simplifying use of the subject index as far as possible, the publishers of Beilstein have always taken great pains in the selection of compound names. To this end, a compromise was chosen between the one extreme of restricting the entry to a single name for each compound, which would require an extensive knowledge of nomenclature and selection rules, and the other extreme of including all the names ever used for a compound, which would make the index expensive and cumbersome.

Over the course of publication of the various Beilstein series, adaptations to meet the changing conventions in international nomenclature have been unavoidable. The most important measure affected the arrangement of prefixes:

H – E III: Arrangement of substitution prefixes in *order of increasing complexity*. (For a list of prefixes used in E III refer to the "blue pages" in the first subvolume of vol. 5 of E III).

E III/IV, E IV: Substitution prefixes arranged in *alphabetical order*. (For a list of prefixes used in E IV refer to the "yellow pages" in the collective subject register of vols. 17/18 of E IV).

Reference to the formula index and the item headings of *related* compounds (also located in the formula index) will frequently be of assistance in tracing the proper designations for a particular compound. Important conventions used in compiling the indexes, in particular the practice used in the indexes of E III and E IV of *inversion of compound names* (arrangement of prefixes behind the parent name) are explained at the beginning of each subject index.

It should be pointed out that the subject indexes do not only contain the names occurring in the item headings but also compound names appearing in *spaced type* in the *text* of the item.

2.1.3 Advantage of the General Indexes (vols. 28, 29)

The general indexes (vol. 28 General Subject Index; vol. 29 General Formula Index) offer a further important advantage:

Having found the desired compound in one of the 27 Beilstein volumes with the help of these indexes, which only contain the contents of the first three handbook series (H – E II, literature up to 1929), it is possible to search further using the system number found there in the volumes of E III and E IV with the same volume numbers. Here additional information on the compound will be found so far as this was dealt with in the literature of the relevant period. This search procedure is further facilitated by the *coordinating references*, previously mentioned in section 1.6, at the top of each odd-numbered page.

2.2 Searching with the Help of the Beilstein System

Should the procedure described in the previous section 2.1.3 not meet with success, it will be necessary to apply the rules of the Beilstein System to determine the volume appropriate for the compound of interest. How these are applied is described in a shortened and highly simplified form in section 2.2.4. The minimum knowledge of the rules required for this purpose are first of all presented in *"condensed form"* (section 2.2.1). The section following (2.2.2) then contains more detailed information on the Beilstein System in the form of the basic rules (G 1 – G 6).

2.2.1 Summary of the Principles of the Beilstein System

[1] The organic compounds taken collectively are distributed over the 27 Beilstein volumes (or groups of volumes) as follows:

cf. p. 16 ff.

Compound Class	Acyclics	Iso-cyclics	Heterocyclics Type and number of ring heteroatoms					
			1 O	2 O, 3 O ...	1 N	2 N	3 N, 4 N ...	1 N, 1 O; 1 N, 2 O ... 2 N, 1 O; 2 N, 2 O ... further hetero-atoms*)
Beilstein Volume Number	1–4	5–16	17/18	19	20–22	23–25	26	27

*) e.g. B, Si, P, but not S, Se, Te (cf. [4], p. 15)

The exact volume allocation is shown in Table 4, p. 19.

Tautomers are classified according to special rules in Beilstein (cf. p. 27 ff.).

Isocyclic Compounds also containing acyclic structural elements are described under isocyclic compounds. cf. p. 16 f.

Heterocyclic Compounds also containing acyclic and/or isocyclic structural elements are described under heterocyclic compounds ("Principle of Latest Possible Systematic Entry").

[2] Further ordering of compounds in Beilstein, *within* the classes given in [1], is determined by the *type* and *number* of *functional groups* presented in Table 4, p. 19. cf. p. 17 ff.

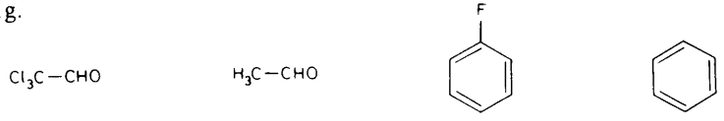
Compounds with the *non-functional* substituents

F, Cl, Br, I, NO, NO_2, N_3

are always described in the same volume as the compounds *without* these substituents.

e.g.

cf. p. 24 f.



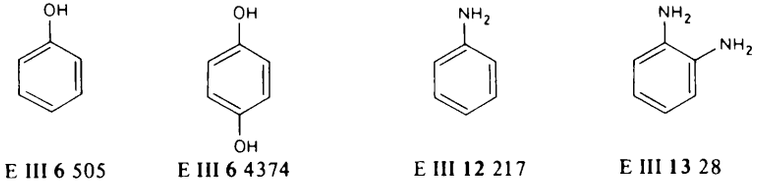
E IV 1 3142*) E IV 1 3094 E III 5 520 E III 5 469

*) Beilstein reference, means here Supplementary Series IV, Vol. 1, p. 3142.

Compounds with several *identical* functional groups follow those which have only *one* such functional group.

e.g.

cf. p. 20

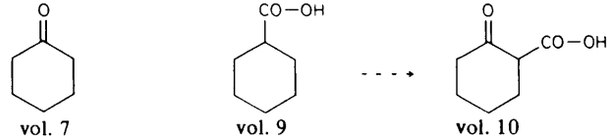


E III 6 505 E III 6 4374 E III 12 217 E III 13 28

Compounds with several *different* functional groups are described in Beilstein at the *"latest possible systematic entry"*, i.e. the functional group with the highest (encircled) number in Table 4, p. 19 is the factor determining its allocation.

e.g.

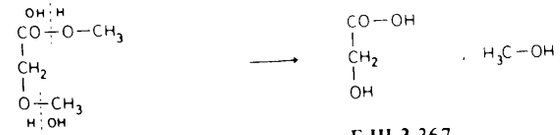
cf. p. 20



vol. 7 vol. 9 vol. 10

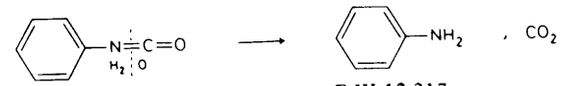
3 Compounds containing one or more *derivatised* functional groups (e.g. –COCl) are considered as *functional derivatives*. These are subjected to a formal hydrolysis and are so reconverted to compounds with free functional groups (e.g. –COOH) which can be located in Beilstein from Table 4, p. 19. The required *derivative* is then described following the systematically latest compound with free functional groups (*registry compound*, cf. p. 17 ff.).

e.g.



E III 3 379 E III 3 367

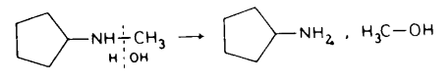
cf. p. 211



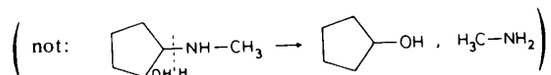
E III 12 903 E III 12 217

Where various routes are available for formal hydrolysis, that route is chosen which leads to the compound described at the *latest possible* place in Beilstein (i.e. in the volume with the *highest possible* volume number).

e.g.



vol. 12

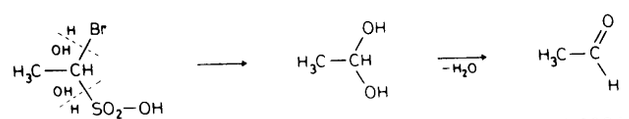


vol. 6

cf. p. 23

Compounds carrying a functional *and* a non-functional group on *one* carbon atom are also subjected to formal hydrolysis.

e.g.



E IV 1 3121 E IV 1 3094

cf. p. 25

4 Organic S, Se and Te compounds are considered in Beilstein as *formal derivatives* of the corresponding oxygen compounds and are described following these.

cf. p. 25

Sulfoxides, sulfones and sulfonium compounds are dealt with after the corresponding sulfides.

cf. p. 26

The principles introduced in this "condensed version" of the Beilstein System are considered in more detail in the following section 2.2.2 and summarised in expanded form in 6 basic rules. These are applied in section 2.2.4 for the systematic search for compounds in Beilstein. (Reference to the literature cited in section 4.2 affords a more detailed description where required.)

2.2.2 Basic Rules of the Beilstein System

The 6 essential rules of the Beilstein System are presented in the following.

G 1. Constitutional Formula

The key to finding an organic compound in the Beilstein Handbook is provided by its *constitutional formula* (structural formula, "valency-bond" formula).

For finding *tautomers*, which may be represented by different constitutional formulae, special rules must be used (see p. 27 ff.).

G 2. The Main Divisions

The organic compounds viewed as a whole are divided into three major groups: the *main divisions* of Beilstein (see Table 3).

Table 3: The Main Divisions of the Beilstein Handbook

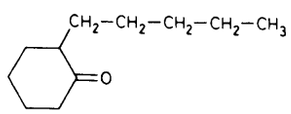
Main Division	Volume Nos.	System Nos.
A. *Acyclic* Compounds	1– 4	1– 449
B. *Isocyclic* Compounds	5–16	450–2358
C. *Heterocyclic* Compounds	17–27	2359–4720

For reasons of clarity the main division "C. *Heterocyclic* Compounds" is further subdivided according to *type* and *number* of *heteroatoms* involved in ring formation, into individual compound classes (1O, 2O, 3O ..., 1N, ...). The ordering of these compound classes in volumes 17–27 is shown in Table 4, p. 19.

G 3. The Principle of Latest Possible Systematic Entry

Even if an isocyclic compound also contains acyclic structural elements it is described with the isocyclic compounds.

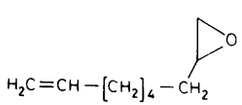
e.g.



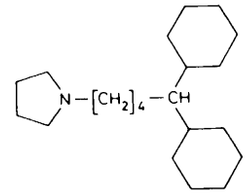
is described in volume 7.

Even if a heterocyclic compound also contains acyclic and/or isocyclic structural elements it is described with the heterocyclic compounds.

e.g.



is described in volume 17.



is described in volume 20.

Thus the location of a compound in Beilstein is invariably determined by that structural element which results in the latest possible systematic entry (higher volume number, higher system number in Beilstein).

This "Principle of Latest Possible Systematic Entry" has general validity for the ordering of compounds in Beilstein.

G 4. Registry Compounds, Functional Groups

The basic structure of the *registry compound* serves as a guide in searching for compounds in Beilstein.

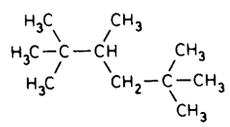
In main divisions A (acyclic compounds) and B (isocyclic compounds), the following are taken as registry compounds:
a) hydrocarbons ("functionless" compounds)
b) hydrocarbons with functional groups.

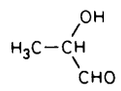
Functional groups as defined in the Beilstein System are restricted to those showing one of the functional features listed in Table 4, p. 19. In contrast to these, the substituents

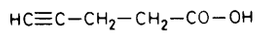
F, Cl, Br, I, NO, NO_2, N_3

are considered as *non-functional* in terms of the Beilstein System; they will be discussed further on (p. 24f.)*).

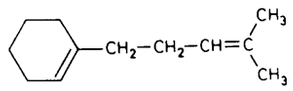
Examples of *acyclic registry compounds:*

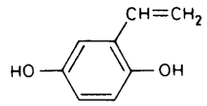


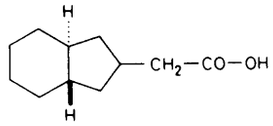




Examples of *isocyclic registry compounds:*





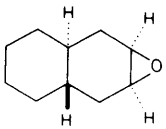


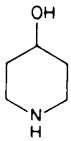
*) Compounds with substituents such as –C≡N, $-\overset{\oplus}{N}\equiv\overset{\ominus}{C}$, –N=C=O are viewed as derivatives in Beilstein (cf. G6, p. 21 ff.).

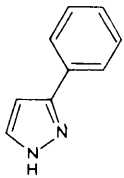
In main division C (heterocyclic compounds) the following are taken as registry compounds:

a) unsubstituted heterocycles,
b) heterocycles with *hydrocarbon residues* as substituents (except on the heteroatom!), } "functionless" compounds
c) heterocycles with *functional groups* (except on the heteroatom!),
d) heterocycles with features of *both* b) *and* c).

Examples of *heterocyclic registry compounds:*







Thus, as shown in Table 4, the main division (or in main division C each of the individual compound classes 1O, 2O, 3O ...), taken together with the type of *functional group(s)* determines unambiguously in which Beilstein volume a registry compound (including all its *derivatives*, see p. 21 ff.) is to be found.

In Table 4, the functional groups from (2) to (17) are arranged in order of increasing rank. This system of ranks determines the order of registry compounds in Beilstein as illustrated in the following example taken from the isocyclic compounds:

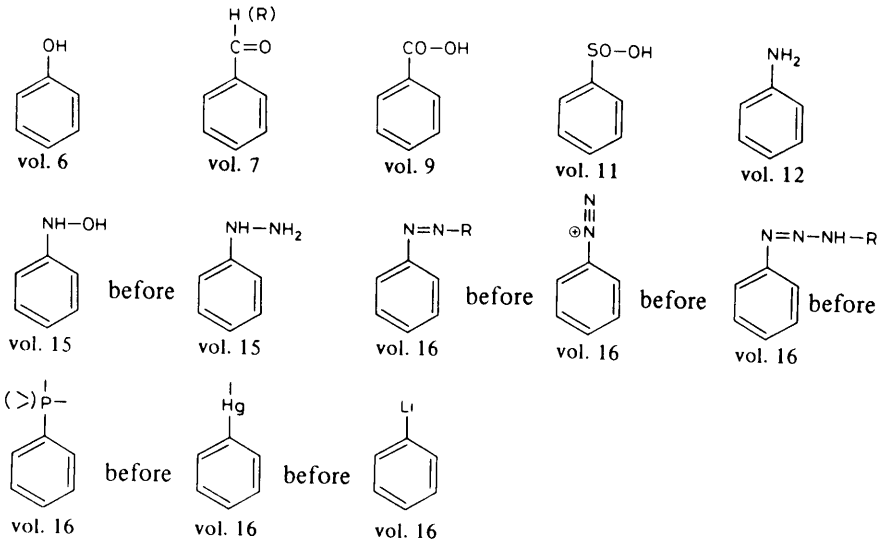
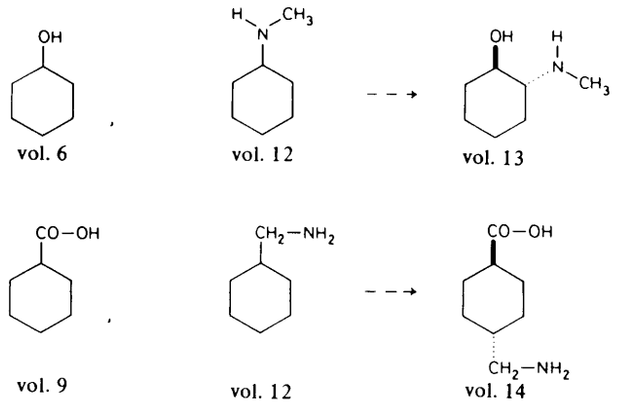


Table 4: Contents of the 27 Volumes of the Beilstein Handbook

	Type of registry compound	Feature of the functional group	Beilstein Volume No. for Main Division: A (Acyclics)	B (Isocyclics)	C (Heterocyclics) Type and number of ring heteroatoms: 1O*)	2O*), 3O*),...,	1N	2N	3N, 4N,...	1N, 1O*), 1N, 2O*),..., 2N, 1O*), 2N, 2O*),..., further heteroatoms**)
1	Compounds without functional groups	–		5			20			
2	Hydroxy-compounds	–OH	1	6	17			23		
3	Oxo-compounds	=O: =O		7			21	24		
		=O: =O + –OH		8						
4	Carboxylic acids	$\leqslant^{O}_{OH}$	2	9						
		$\leqslant^{O}_{OH}$: $\leqslant^{O}_{OH}$ + –OH; $\leqslant^{O}_{OH}$ + =O; $\leqslant^{O}_{OH}$ + =O + –OH	3	10						
5	Sulfinic acids	$-SO_2H$								
6	Sulfonic acids	$-SO_3H$								
7	Seleninic acids, Selenonic acids, Tellurinic acids	$-SeO_2H$ and $-SeO_3H$; $-TeO_2H$	4	11	18	19	22	25	26	27
8	Amines	$-NH_2$: $-NH_2$		12						
		$-NH_2$: $[-NH_2]_n$; $-NH_2$ + –OH		13						
		$-NH_2$: $-NH_2$ + =O; $-NH_2 + \leqslant^{O}_{OH}$; $-NH_2$ + ...		14						
9	Hydroxylamines and Dihydroxyamines	$-NH-OH$; $-N<^{OH}_{OH}$								
10	Hydrazines	$-NH-NH_2$		15						
11	Azo-compounds	$-N=NH$								
12	Diazonium compounds	$-N\equiv N]^{\oplus}$								
13	Compounds with groups of 3 or more N-atoms	$-NH-NH-NH_2$, $-N(NH_2)_2$, $-N=N-NH_2$, etc.								
14	Compounds containing carbon directly bonded to P, As, Sb, and Bi	e.g. $-PH_2$, $PH-OH$, $-P(OH)_2$, $-PH_4$,..., $-PO(OH)_2$		16						
15	Compounds containing carbon directly bonded to Si, Ge, and Sn	e.g. $-SiH_3$, $-SiH_2(OH)$, ...								
16	Compounds containing carbon directly bonded to elements of the 3rd–1st A-groups of the	e.g. $-BH_2$, $-BH(OH)$, ..., $-Mg^{\oplus}$								

If a registry compound contains several *different functional groups*, the compound is to be found at the *"latest possible systematic entry"*, i.e. the functional group resulting in the latest possible classification is the deciding factor for locating a registry compound in Beilstein.

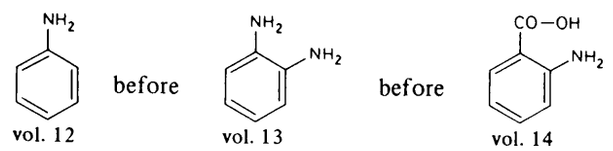
e.g.



G 5. Additional Rules for Ordering Registry Compounds

The following additional criteria further determine the sequence of registry compounds and thus their location in the Beilstein Handbook. They are considered here briefly with examples:

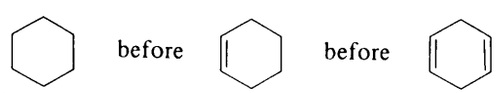
a. The *Type* and *Number* of the *Functional Groups:*



For the sequence within a volume the following are important:

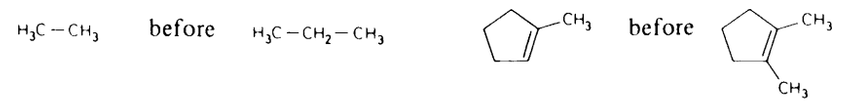
b. The *Degree of Saturation:*

E IV 1 900 E IV 1 1063



E IV 5 27 E IV 5 218 E IV 5 385

c. The *Number* of *Carbon Atoms*



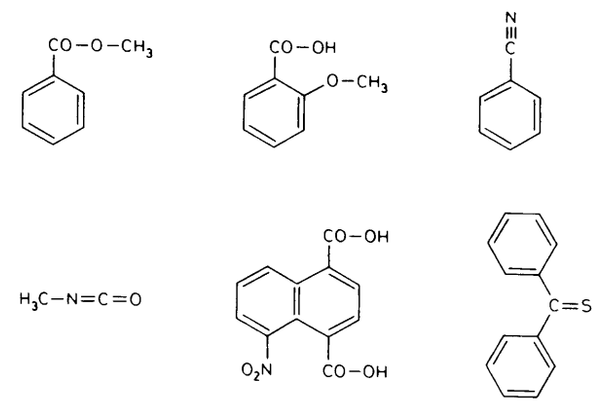
E IV 1 108 E IV 1 176 E IV 5 239 E IV 5 254

The more detailed classification of the registry compounds listed in Table 4 will not be considered further here, since this may be inferred from the table of contents of the individual Beilstein volumes. (For a more detailed discussion, reference should be made to the list cited in section 4.2).

G 6. Derivatives

If a compound is to be considered as a registry compound it may *only* contain substituents listed in Table 4 as functional groups. All other compounds are considered as *derivatives* of registry compounds and are dealt with following these.

Examples of Derivatives



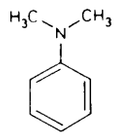
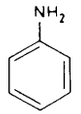
Three types of derivatives are distinguished:

1. **Functional Derivatives,**
2. **Substitution Products,**
3. **Chalcogen Analogues.**

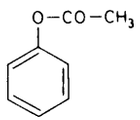
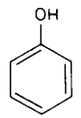
The three different types of derivatives of a registry compound are dealt with successively in this order in Beilstein.

1. *Functional Derivatives*

are compounds containing the functional groups listed in Table 4, p. 19 in derivatised (chemically modified) form.

e.g.  is a *functional derivative* of 

$H_3C-SO_2-NH_2$ is a *functional derivative* of H_3C-SO_2-OH

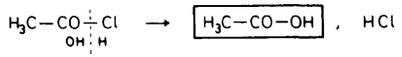
 is a *functional derivative* of 

$H_3C-N=C=O$ is a *functional derivative* of H_3C-NH_2

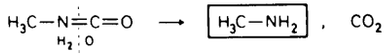
To find a compound of this type in Beilstein it is subjected to *hydrolysis*, which leads to the *registry compound* and its coupling component(s)*) (the term "hydrolysis" as used here is purely formal and is not to be taken in a strict chemical sense). Such a formal hydrolysis may have to be performed several times in order to arrive at the required registry compound; in this procedure the OH-group of the water molecule is coupled to a *C-atom* wherever possible.

If only a single carbon containing compound is formed on hydrolysis this is to be considered as the *registry compound;* if several are formed, the *registry compound* is taken as that which is systematically classified at the latest possible place (highest volume number; *"Principle of Latest Possible Systematic Entry"*).

e.g. (The compound in the "box" is the *registry compound* in each case, the remaining substances to the right of the arrow are the coupling components).

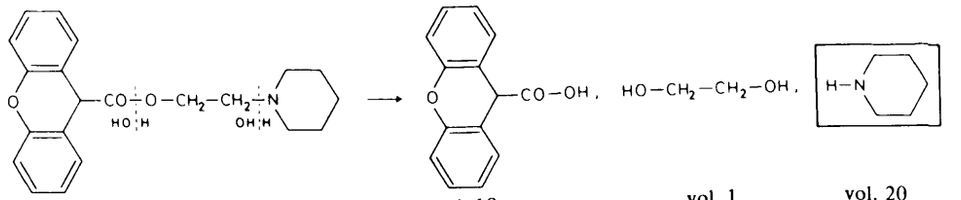


vol. 2

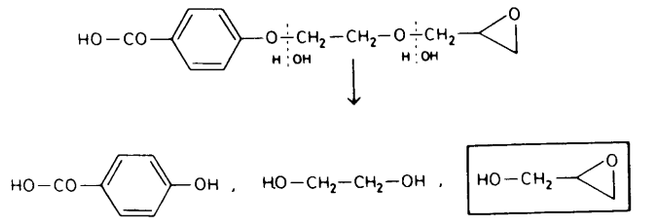


vol. 4

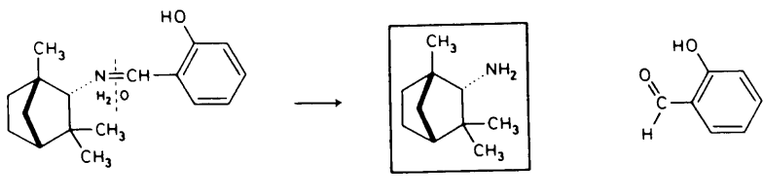
*) Occasionally further formal operations are necessary to obtain the fundamental registry compound, cf. p. 29 and scheme 1, p. 31.



vol. 18 vol. 1 vol. 20



vol. 10 vol. 1 vol. 17

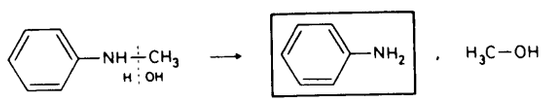


vol. 12 vol. 8

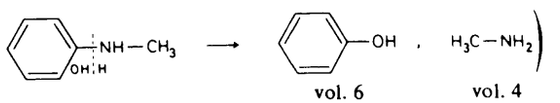
($-NH_2$ leads to later classification than =O and –OH!)

If several different possibilities of formal hydrolysis are available the one leading to the systematically latest registry compound is selected.

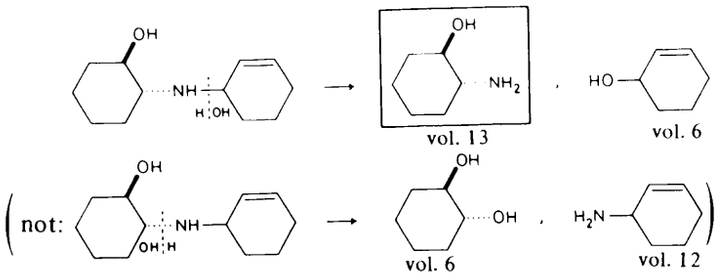
e.g.



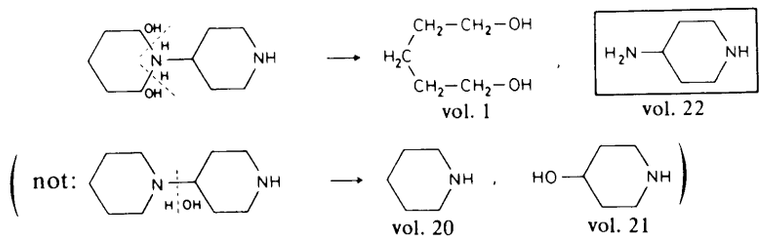
vol. 12 vol. 1

(not: )

vol. 6 vol. 4



($-NH_2$ *and* $-OH$ together lead to later classification than $2 \times -OH$ or $-NH_2$ *alone*!)



($-NH_2$ leads to later classification than $-OH$)

Important note:

Sulfoxides and Sulfones may *not* be subjected to formal hydrolysis; they are described in Beilstein following the corresponding sulfides (cf. p. 26).

2. *Substitution Products*

are compounds containing one or more of the following so-called *non-functional substituents*

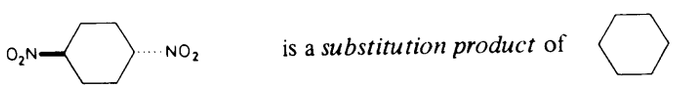
F, Cl, Br, I, NO, NO_2, N_3

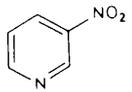
The substitution products of a registry compound are dealt with successively, in this order, in Beilstein.

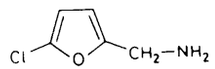
e.g.

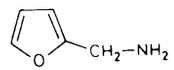
CCl_4, $CH_2(NO_2)_2$, CH_3-N_3 are *substitution products* of CH_4

$ClCH_2-CO-OH$ is a *substitution product* of $H_3C-CO-OH$


is a *substitution product* of


is a *substitution product* of

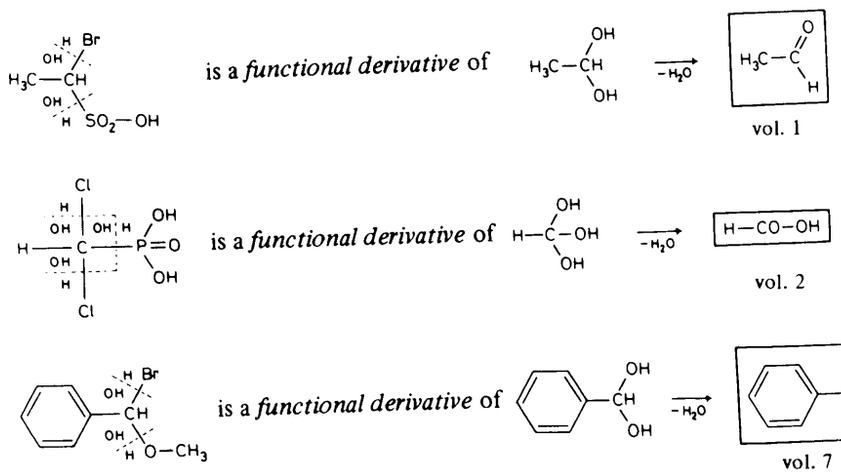

is a *substitution product* of



To locate a compound recognised as a substitution product in Beilstein, the non-functional substituents must be replaced by H-atoms in order to determine the required registry compound*).

If however a compound should possess on *one* C-atom (i.e. a geminal arrangement), not only a free (or chemically modified) functional group, but also one or more non-functional substituents, then these compounds are considered as *functional derivatives* for the purpose of determining the relevant registry compound, i.e. they are subjected to a formal *hydrolysis*.

e.g. (registry compounds shown in "boxes")



3. *Chalcogen Analogues*

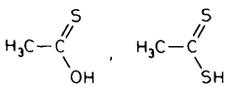
Organic sulphur, selenium and tellurium compounds are considered as *derivatives* (chalcogen analogues) of the corresponding oxygen compounds, obtained by formally substituting oxygen for the (bivalent) sulphur, selenium or tellurium atoms.

*) See footnote p. 22.

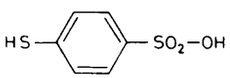
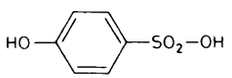
e.g.

is a *chalcogen analogue* of

H_3C-SH , H_3C-SeH are *chalcogen analogues* of H_3C-OH

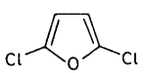

are *chalcogen analogues* of $H_3C-CO-OH$

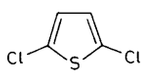
$C_2H_5-NH-SH$ is a *chalcogen analogue* of $C_2H_5-NH-OH$


is a *chalcogen analogue* of


To locate such chalcogen analogues in Beilstein the bivalent chalcogen atoms must be replaced by oxygen to obtain the relevant registry compounds*). The items on chalcogen analogues are to be found in the same volume as those of the corresponding oxygen compounds.

e.g.


E III/IV 17 230


E III/IV 17 243

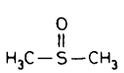
C_2H_5-OH
E IV 1 1289

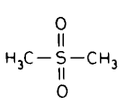
C_2H_5-SeH
E IV 1 1411

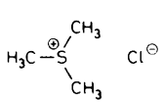
Sulfoxides and sulfones
as well as sulfonium compounds follow the corresponding sulfides in Beilstein.

e.g.

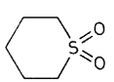
$H_3C-S-CH_3$
E IV 1 1275


E IV 1 1277


E IV 1 1279


E IV 1 1280

E III/IV 17 51


E III/IV 17 55

*) See footnote p. 22.

2.2.3 The Filing of Tautomers in Beilstein

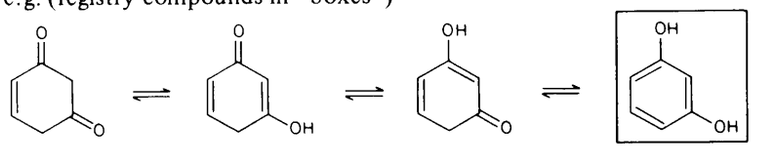
The classification of tautomeric compounds, consisting of two or more readily interconvertible forms with *different constitutional formulae* ("valency-bond" formulae), requires additional rules since the locations of the individual tautomeric forms within Beilstein are frequently widely separated.

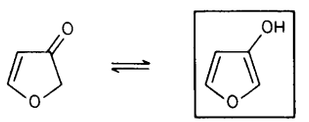
The following rules hold for the most important class of tautomers, *oxo-enol tautomers:*

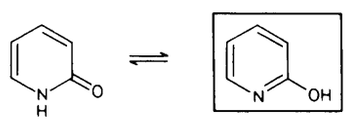
a) The *enol-form* determines the location of the entry if the OH-group is bonded to a *benzenoid ring*, on condition that, the carbon atom bearing the OH-group has *no adjacent heteroatom*, pyridine rings excepted.

The term *"benzenoid"* is used for rings with 6 π-electrons excluding the middle rings of linearly condensed polynuclear compounds.

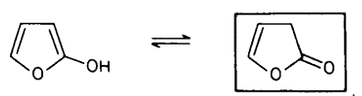
e.g. (registry compounds in "boxes")

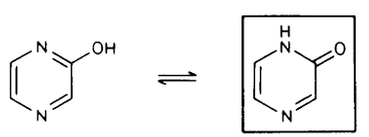


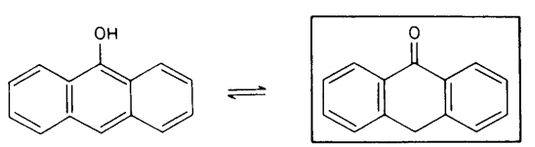




but:

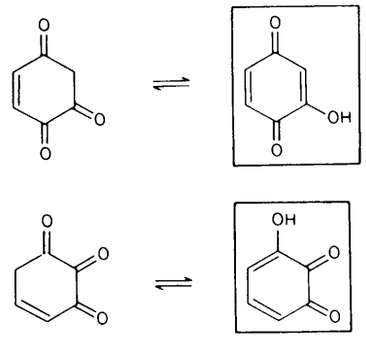






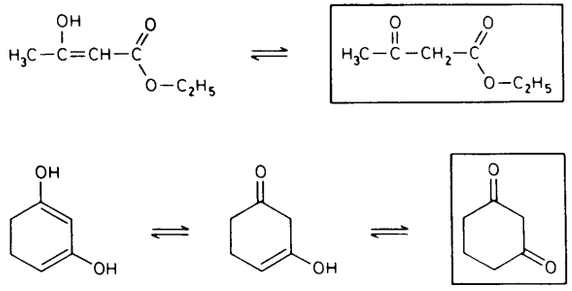
b) The *enol-form* also determines the location of the entry where the OH-group is attached to a *quinoid ring.*

e.g. (registry compounds in "boxes")



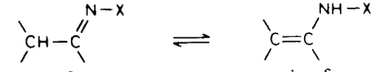
c) In all other cases the *oxo-form (keto-form)* determines the location of the entry in Beilstein.

e.g. (registry compounds in "boxes")



The rules discussed above for the *oxo-enol tautomerism* do not apply for functional derivatives obtained from the individual tautomers where these no longer possess readily delocalised protons; for example, an enol-ether in Beilstein follows the position at which the free enol would have been dealt with, although the enol itself is considered elsewhere (along with the corresponding "oxo-compound", see above c.).

For classifying *imino-enamine tautomers,*



imino-form enamine-form

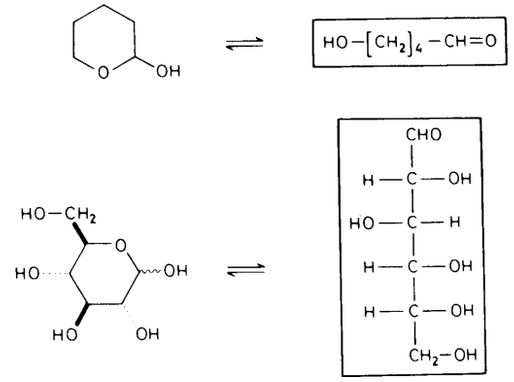
(X = H, OH, NR_2, etc.)

rules analogous to a) – c) above hold.

Oxo-cyclo tautomerism:

The location of the entry is *invariably* determined by the *oxo-form (acyclic form).*

e.g. (registry compounds in "boxes")



2.2.4 Procedure for Searching for Compounds in Beilstein

Application of the generalised procedure given in scheme 1 on p. 31 enables the volume relevant for the required compound to be determined. This procedure is based on the essential rules G 1 to G 6 summarised in section 2.2.2.

Note: The bracketed plus-sign (+) in scheme 1 is intended to convey that the compound being searched for may be a derivative in which *several* of the given types of derivatisation occur; if this should be the case, *several* of the manipulations mentioned in scheme 1 (hydrolysis, replacement of substituents by H, replacement of S, Se, Te by O) will be necessary.

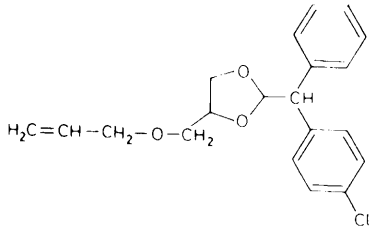
The general procedure for determining the Beilstein volume relevant for a particular compound, presented in shortened form in scheme 1, will now be considered in terms of a specific example.

The compound to be searched for in Beilstein is:

4-allyloxymethyl-2-(4,4'-dichlorobenzhydryl)-(1,3)dioxolane,

empirical formula: $C_{20}H_{20}Cl_2O_3$.

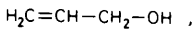
No entry with this empirical formula is to be found in the general formula index (vol. 29); this implies that this compound had not been described up to 1929. Scheme 1 will therefore be applied to find the required compound in Beilstein.



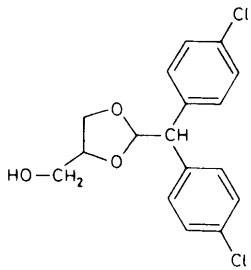
1

Inspection of this constitutional formula reveals that tautomerism is not possible here. The presence of the acyclic ether group, together with the two chlorine atoms attached to the benzene nuclei, show that the compound is a *derivative* rather than a registry compound. Following scheme 1 it is recognised that two types of derivative formation are involved: in terms of the acyclic ether group, compound **1** is a *functional derivative,* in terms of the two chlorine atoms it may be viewed as a *substitution product* simultaneously.

In accordance with scheme 1 a formal hydrolysis of the compound is first carried out. This results in the following compounds:



2

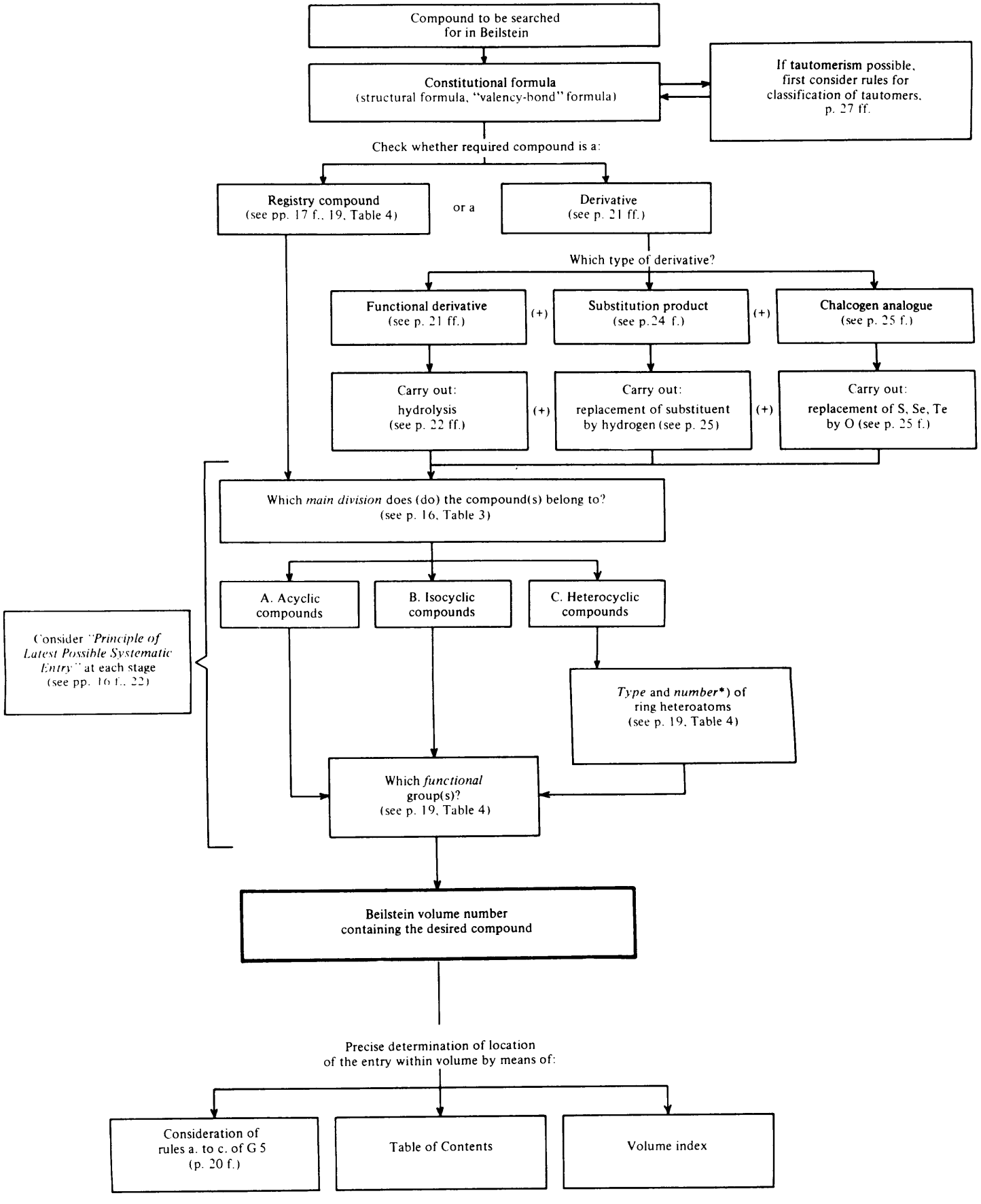


3

According to the previously mentioned *"Principle of Latest Possible Systematic Entry",* the search procedure may now be continued with the *main component* only, i.e. with the component appearing later in Beilstein (higher volume number, higher system number), hence, in this case with compound **3**.

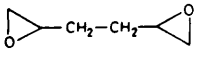
In the next step, the two chlorine atoms, as *non-functional substituents,* are replaced by hydrogen atoms, thus giving compound **4**.

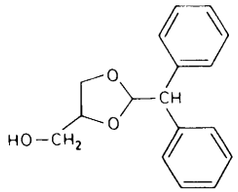
Scheme 1: General procedure for determining the Beilstein volume relevant for a particular organic compound



*) The ring heteroatoms may be contained in *one* ring or may be distributed over *several* rings, e.g. the compounds

and





4

Further manipulations with compound **4** are not required. The question as to the *main division* in scheme 1 is now easily answered: compound **4** (and hence the required compound **1** also) belongs to main division "C. *Heterocyclic* Compounds" i.e. compound **1**, if known in the literature, is to be found in one of the volumes 17 to 27. This range is narrowed further by the assignment to compound class 2 O carried out in the next step (cf. p. 19, Table 4). The compound of interest must thus be located in vol. 19.

Since the only *functional group* contained in the fundamental *registry compound* **4** is an alcoholic OH-group, compound **1** is readily assigned with the help of Table 4, p. 19 to the group "(2) *Hydroxy Compounds*". Since the lower the number of a registry compound (together with its derivatives), the earlier its appearance in Beilstein, the compound **1** will appear relatively "early" in volume 19, i.e. it will be found in one of the first subvolumes.

The simplest means of more exactly determining the location of the entry of the required compound within volume 19 is to look through the table of contents. In the present example, the table of contents of volume 19/2 reveals that compound **1** is to be found in this subvolume, to be more exact, under "II. *Hydroxy-Verbindungen*, A. *Monohydroxy-Verbindungen*".

The subclassification in the table of contents according to degree of saturation, refers to the fundamental registry compound, hence in this case to compound **4**. This has the empirical formula $C_{17}H_{18}O_3$, which corresponds to the general empirical formula $C_nH_{2n-16}O_3$. Accordingly, compound **1** is to be found in subsection "9. *Monohydroxy-Verbindungen* $C_nH_{2n-16}O_3$" between pages 899–919. The intermediate headings given in the text (here: "Hydroxy-Verbindungen ...") now easily enable the required compound to be finally located on page 911 (with system number 2699).

A search in the formula index naturally leads to the same result: as soon as the correct subvolume (here 19/2) has been found with the help of the table of contents, the empirical formula, here $C_{20}H_{20}Cl_2O_3$, can be looked up in the formula index at the end of the subvolume, which then refers to the same entry (here p. 911).

With the given system number (here 2699) it will also be possible to find compound **1** in supplementary series to be published in the future provided new findings are published in the primary literature.

The reader who has practised the procedure exemplified above a few times using scheme 1, will have no difficulty in finding the location of entry of a required compound in Beilstein, provided of course the compound was dealt with in the literature during the period in question.

3 The History of Beilstein

In a few years time *Beilsteins Handbuch der Organischen Chemie* will be celebrating its centenary: The first edition of Beilstein appeared in the years 1881–1882 as two subvolumes, in which around 15,000 carbon compounds were described on 2,200 pages. Evaluation of the literature and editorial treatment for this first edition and the two subsequent editions, which rapidly followed, was managed single-handed by *F. K. Beilstein*, whose name the handbook bears.

F. K. Beilstein was born the son of German parents in St. Petersburg in 1838; after the study of chemistry in Heidelberg, Munich and Göttingen he was called to the Chair of Chemistry at the Imperial Technological Institute in St. Petersburg where he succeeded Mendeleev. Here, plans to publish a handbook of organic chemistry rapidly matured, a task which was to occupy him fully for 40 years, until his death in 1906.

The immense success of the 1st edition of his handbook soon compelled him to publish a 2nd edition, which appeared in the years 1885–1889 and extended to three volumes with 4,080 pages. Between 1892 and 1906 the third edition then appeared, together with a supplementary series and a complete index for the 3rd edition. These 8 volumes, including the supplementary series, contained critically reviewed material on all the then known carbon compounds on around 11,000 pages.

Even before work had been completed on the 3rd edition, Beilstein realised that publication of a handbook of this type exceeded the working capacity of any one individual. He thus handed the work of further publication over to the German Chemical Society, which, under the editorship of P. Jacobson and B. Prager started on publication of the 4th edition in 1918. In 1933 F. Richter took over the editorship followed by Hans-G. Boit, who was publisher of the handbook and director of the Beilstein Institute in Frankfurt/Main from 1961 until March 31st, 1978. From April 1st, 1978 Reiner Luckenbach is the managing director of the institute.

The "Beilstein-Institut für Literatur der Organischen Chemie", which adopted the legal status of a trust in 1951, is engaged, in close cooperation with the Springer-Verlag (Berlin–Heidelberg–New York), today as in the past, in the rapid publication of the supplementary series of Beilstein.