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ORGANIC CHEMISTRY DIVISION  
COMMISSION ON PHYSICAL ORGANIC CHEMISTRY\*

## NOMENCLATURE FOR ORGANIC CHEMICAL TRANSFORMATIONS

(Recommendations 1988)

*Prepared for publication by*

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# Nomenclature for organic chemical transformations (Recommendations 1988)

## Abstract

These rules provide a general system of nomenclature for transformations whereby one organic compound is converted into another. A *transformation* is distinct from a *reaction* in that it describes only those changes that are involved in converting the structure of a substrate into that of a product, regardless of the reagent or the precise nature of the substrate, or (with some exceptions) the mechanism. Thus all processes in which X—H is converted into X—NO<sub>2</sub> are examples of the single transformation called "nitration", whatever the nature of X, and irrespective of whether the reaction entails the replacement of H<sup>+</sup> by NO<sub>2</sub><sup>+</sup>, of H<sup>•</sup> by NO<sub>2</sub><sup>•</sup>, or of H<sup>-</sup> by NO<sub>2</sub><sup>-</sup>.

The basis of the names of all transformations is that they provide a description of the conversion of substrate into product by giving a string or strings of the names of groups or entities that become attached to and/or detached from the substrate, followed by a suffix that describes the nature of the transformation. Straightforward examples are self-explanatory; for example: "hydro,chloro-addition"; "dibromo-elimination"; "hydroxy-de-iodo-substitution". For many transformations, particularly substitutions, simplified names are recommended for use in speech or writing (by contrast to the more detailed indexing names). Thus "hydroxy-de-iodination" may be used instead of "hydroxy-de-iodo-substitution", or "nitration" instead of "nitro-de-hydro-substitution". A list of non-systematic names is given for transformations that are too complex to be named by the present systematic rules.

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## PREAMBLE

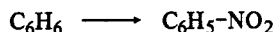
### 1 Introduction

These recommendations provide a general system of nomenclature for transformations whereby one organic compound is converted into another. Except for substitution transformations, for which systematic names have been employed since 1954<sup>1</sup>, these processes have lacked systematic verbal representation. Some have been characterised either as "name reactions" (e.g., Michael reaction) or by various and sometimes inconsistent descriptive terms but often they have been represented only by an equation or a relatively cumbersome multi-word description.

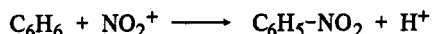
Several transformations have well-established non-systematic names, for example "hydration", "lactonization", "hydrolysis". It is not intended that the names defined by the present recommendations should displace these common terms. However, many such names are used erroneously ("hydrogenation" in place of "hydrogenolysis") or ambiguously ("bromination" for both substitutions and additions), and it is desirable that such confused usage should be discontinued.

A *transformation* must be distinguished from a *reaction*. The full description of a reaction would state or imply all the reactants used and all the products formed. In a transformation one is concerned only with changes in one particular species designated as the "substrate" (see below). Thus, "nitration" refers to a process in which a hydrogen atom of substrate X—H is replaced by a nitro group to give X—NO<sub>2</sub>, irrespective of whether the reagent is HNO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, NO<sub>2</sub><sup>+</sup>BF<sub>4</sub><sup>-</sup> or EtONO<sub>2</sub>.

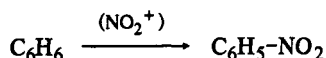
In representing a transformation the substrate should appear alone on the left of the arrow that denotes the change, and only products that are described by the transformation should appear to the right. For example:



A representation of the following type describes a reaction and should not be used for a transformation:



In this document, when it is desired to draw attention to a reagent its formula is placed in parentheses over the arrow:



### 2 Classes of transformations

In the development of these recommendations, it was necessary to recognize several classes of transformations. Classes recognized and defined here briefly<sup>2</sup> include the following:

**Attachments**, in which the substrate species becomes attached to another species through covalent bond formation at a single atom of each species, without loss of any atom or group from the substrate.

**Detachments**, in which the substrate species loses a fragment through rupture of a single or multiple covalent bond between two atoms, without the acquisition of any other atom or group.

**Substitutions**. In univalent substitutions a univalent atom or group replaces a univalent atom or group. In multivalent substitutions, a multiply-bonded atom or group or more than one atom or group is replaced by a multiply-bonded atom or group or more than one atom or group.

**Additions**, in which one or more pairs of atoms or groups, alike or unlike within any pair, become attached to different atoms of an unsaturated substrate or to a single substrate atom as in a carbene or nitrene. In contrast to a usage sometimes employed, transformations in which one chemical species becomes attached to another through covalent bond formation between a single atom of one and a single atom of the other are called *attachments*, not additions.

**Eliminations**, in which two or more atoms or groups are detached from different positions of a substrate so as to form or extend an unsaturated system, or from a single site so as to form a carbene, nitrene or similar entity. In contrast to a usage sometimes employed, transformations in which one chemical species fragments into two by rupture of the covalent linkage between two atoms are called *detachments*, not eliminations.

**Simple rearrangements**, in which a group changes its point of attachment, whether or not accompanied by any other transformation.

**Insertions**, in which a divalent atom or group is inserted between two covalently bonded atoms to form a product in which those two atoms are bonded to the inserted atom or group.

**Extrusions**, in which two atoms covalently bonded to an atom or group become bonded directly to each other with concomitant loss of the previously interposed atom or group.

Besides these rather simply defined categories, there are some which, although chemically no more complex, pose special problems of nomenclature. These include *ring-opening* and *ring-closing* transformations, and also *coupling* and *uncoupling* transformations, in which identical moieties become joined or separated with the concomitant loss or gain of other atoms or groups.

Moreover, some transformations are of such chemical complexity as to make the systematic naming of them a formidable and possibly unprofitable task. Such complex transformations are collected in a list of non-systematic but carefully defined names.

### 3 Recognition of the "substrate"

When two or more chemical species are involved in a reaction, it is often obvious which should be designated the "substrate", that is, the principal substance on which the other reagent(s) are considered to operate. In other cases it is less obvious. Thus, in the reaction of aniline with benzoyl chloride to form *N*-phenylbenzamide, either reactant seems an equally probable choice as substrate. This single *reaction* comprises two distinct *transformations*: replacement of the chlorine atom of benzoyl chloride by an anilino group, and of a hydrogen atom of aniline by a benzoyl group. These recommendations provide separate names for the two transformations, and do not attempt to name the reaction as a whole. The choice of which transformation to name, which is equivalent to choosing one reactant as the substrate, is made with reference to the context.

It is a cardinal principle of these recommendations that the name of the transformation is independent of the nature of the substrate. Thus *any* transformation in which an X—H bond is replaced by an X—NO<sub>2</sub> bond is "nitration".

### 4 Desirable characteristics in names

Two rather different purposes are served by systematic names for transformations. One is indexing and the retrieval of information, and the other communication in speech and writing. Rather different criteria need to be met if names are to be satisfactory for the two purposes.

For indexing, names must be definitive. Though simplicity in a name is always a virtue, there is no requirement that indexing names be short, or that they avoid interposed letters or numbers; also, they may use punctuation marks to specify certain types of information.

Names for use in speech should be relatively short and euphonious, and should contain features distinctive to the ear. They should be easily adapted into other major languages of science. Ideally the names for specific transformations should be precise, but some sacrifice of precision can be tolerated in order to satisfy the above criteria if no serious ambiguity results. A name that is difficult to pronounce or for the ear to comprehend is likely to be avoided in speech, and is therefore of little worth for oral communication. Names for use in effective written discourse must meet similar criteria, for similar reasons.

For either purpose, there is need both for specific names that portray single transformations and for generic names that portray sets of closely related transformations. Thus, there is need for a name to represent the category of substitution reactions in which an alkoxy group replaces a halogen atom, but also for a name to represent the specific case in which an ethoxy group replaces a bromine atom. These recommendations provide for both.

Some of the transformations falling within the scope of these recommendations are of such complexity that even the "speech/writing" names for them are too unwieldy to be of other than limited value unless visual aid is also provided (e.g. Example 2 of Rule 8.5.3). Such limitations are recognized and are inherent in the application of any rules of systematic chemical nomenclature.

## 5 Site designation

In the naming of transformations it is often necessary to designate the *relative* locations of reacting sites of substrates. The commonly used indices for reacting sites are Greek letters and arabic numerals, but use of either to designate relative sites can in particular cases lead to ambiguities. Thus, it could be confusing to speak of 1,4-addition to the 9- and 10-positions of anthracene, or  $\alpha,\alpha$ -elimination from the  $\beta$ -position of  $\beta$ -bromostyrene. Accordingly these recommendations employ for relative site designation post-slashed arabic numerals. Instead of writing "1,4-dibromo-addition" the *relative* nature of the site designations is indicated by writing "1/4/dibromo-addition". In speech the slash symbols are not pronounced.

In casual speech and writing one may wish to refer to a specific substrate and to modify the site designations accordingly, using absolute rather than relative numbering. For example the 1/4/dibromo-addition to 2,4-hexadiene could be called "2,5-dibromo-addition". Such usage, however, violates the principle enunciated above that the name of a transformation is independent of the substrate and it is therefore not a formal part of the nomenclature.

The elements of the reacting sites of substrates are denoted by italicised atomic symbols, as in *O,C*-dihydro-addition (to a carbonyl group). For transformations involving only carbon sites the atomic symbols are omitted. Where relative site numbers and atomic symbols are both used, the symbol is placed after the slash - for example, 1/0,3/*N*-dihydro-addition (to an azoxy compound).

## 6 Mechanistic information

The naming of transformations is distinguished from the designation of *reaction mechanisms*. Often two or more distinctly different mechanisms for the same transformation are indicated by experimental evidence, or are conceivable, and views as to what mechanism prevails may be in dispute or may change with time. The names for transformations provided by these recommendations do not include information about reaction mechanism. For example, one could hypothesise that the conversion of benzene to nitrobenzene entails the replacement of  $H^+$  by  $NO_2^+$ , of  $H^+$  by  $NO_2^+$ , or even of  $H^-$  by  $NO_2^-$ . In each case the *transformation* is the same. The chemist who wishes to indicate a mechanism can do so by adding appropriate parenthetical adjectives or phrases; e.g., "nitration (via nitronium ions)", but such amplification is not a formal part of the nomenclature. (See examples 10 and 11 under Rule 1.1.) Similarly the stereochemical aspects of a transformation are not formally part of the name, but may be incorporated parenthetically as, for example, in "(*syn*)dibromo-addition". (See examples 4 and 5 under Rule 2.1.1.)

One type of mechanistic information should, however, be acknowledged in the naming of transformations. That is knowledge of what bonds break or form during a reaction. For example, to name the hydration of benzonitrile to benzamide as though it involved replacement of the cyano group by a carboxamido group would be a travesty. The name given to a transformation should be in accord with knowledge as to the changes of connectivity that occur.

In some cases the same overall result may be achieved by quite different means. Thus, transformation of allyl benzoate to propyl benzoate can be performed either by dihydroaddition (of  $H_2$ ) to the olefinic linkage, or by propoxy-de-allyloxylation (with propanol). To name these two processes identically would be more detrimental than helpful.

Subtle variations in reaction conditions can sometimes alter the pattern of connectivity change. Thus, 1-methyl-2-butenyl hydrogen phthalate is hydrolyzed in weakly alkaline solutions with scission of the alkyl-oxygen bond but in concentrated alkaline solutions with scission of the acyl-oxygen bond. In such a case one might wish to employ different names for the transformation to distinguish different routes, or one might justifiably use either name if distinguishing between them happened not to be important in a particular context, or not feasible.

## 7 Naming entities and groups

A transformation may involve one or more attachments or detachments of entities to or from a substrate. Some transformations can be accurately described only by specifying the oxidation level of an entity. For example, the attachment of  $NO_2^+$  to benzene to form a cationic Wheland intermediate is a different transformation from the attachment of  $NO_2^+$  to form  $C_6H_6NO_2^+$ . It is therefore necessary to use different names for the different oxidation levels ( $NO_2^+$ , nitylium or nitronium;  $NO_2^+$ , nityl;  $NO_2^-$ , nitrite). On the other hand, as discussed above in section 6, "Mechanistic Information", some transformations (substitutions, additions, eliminations) can in principle be accomplished by reagents of different oxidation levels. In naming these transformations an entity should if possible be given a name that does not specify the oxidation level (nitro, for example) so as not to imply a particular mechanistic path. In such a case the entity is referred to as a "group". Tables 1 - 4 give illustrative lists of names of entities and groups: it will be seen that suitably distinctive names are not always available.

## 8 Provisional publication

Some of these recommendations, namely, those dealing with univalent substitution, addition and elimination transformations, were provisionally published in 1981<sup>3</sup>.

TABLE 1. An illustrative list of names of entities of specified oxidation level and of groups of unspecified oxidation level \*

X	cation (X <sup>+</sup> )	radical (X <sup>•</sup> )	anion (X <sup>-</sup> )	group (X-)
H	hydron	hydrogen <sup>†</sup>	hydride	hydro
CH <sub>3</sub>	methylum	methyl	methanide	methyl
C <sub>6</sub> H <sub>5</sub>	phenylum	phenyl	benzenide	phenyl
CN		cyanyl <sup>‡</sup>	cyanide	cyano (-CN) isocyano (-NC)
CH <sub>3</sub> CO	acetylum or ethanoylium	acetyl or ethanoyl	1-oxoethanide	acetyl or ethanoyl
HOCO	carboxylium	carboxyl	carboxylide	carboxy
CH <sub>3</sub> CO <sub>2</sub>	acetoxylum or ethanoyloxylium	acetoxyl or ethanoyloxy	acetate or ethanoate	acetoxy or ethanoyloxy
H <sub>2</sub> N	aminylum	aminyl	amide	amino
C <sub>6</sub> H <sub>5</sub> NH	phenylaminylum	phenylaminyl	phenylamide	phenylamino or anilino
H <sub>2</sub> N-NH	hydrazinium or hydrazylum	hydrazinyl or hydrazyl	hydrazinide or hydrazide	hydrazino
N <sub>3</sub>		azidyl	azide	azido
NO	nitrosylium or nitrosonium	nitrosyl		nitroso
NO <sub>2</sub>	nitrylium or nitronium	nitryl	nitrite	nitro (-NO <sub>2</sub> ) nitrito or nitrosooxy (-O-NO)
HO	hydroxylium	hydroxyl	hydroxide	hydroxy
CH <sub>3</sub> O	methoxylium	methoxyl	methoxide	methoxy
OCN			cyanate	cyanato (-CNO) isocyanato (-NCO)
F	fluoranylium	fluorine <sup>†</sup>	fluoride	fluoro
HS	sulfanylium	sulfanyl	sulfanide	sulfanyl or mercapto
CH <sub>3</sub> S	methylsulfanylium	methylsulfanyl	methylsulfanide	methylthio or methylsulfanyl
CH <sub>3</sub> SO <sub>2</sub>	methanesulfonylium	methanesulfonyl	methanesulfinate	methylsulfonyl
HOSO <sub>2</sub>	hydroxysulfonylium	hydroxysulfonyl	hydrogen sulfite	sulfo
ClSO <sub>2</sub>	chlorosulfonylium	chlorosulfonyl	chlorosulfite	chlorosulfonyl
CH <sub>3</sub> SO <sub>3</sub>	methanesulfonyloxylium	methanesulfonyloxy	methanesulfonate	methylsulfonyloxy

\* Many of these names are based on draft recommendations currently being prepared by the Commissions on the Nomenclature of Inorganic and Organic Chemistry, II.2 and III.1 respectively.

<sup>†</sup> Strictly these names should be monohydrogen, monofluorine, but the simpler alternatives are normally adequate.

<sup>‡</sup> In naming some transformations it may be desirable to name an entity as if it had the structure of a specified canonical form: thus, if the cyanyl radical attaches to a substrate via the nitrogen atom, the name "isocyanyl" may be used (see Rule 4.1.1 and Examples 8 and 10 thereunder).

TABLE 2. An illustrative list of names of charged groups of unspecified oxidation level and of some related entities of specified oxidation level.

-CH <sub>2</sub> <sup>-</sup>	methanidyl		
-CO <sub>2</sub> <sup>-</sup>	carboxylato	CO <sub>2</sub>	carbon dioxide
-NH <sup>-</sup>	amidyl		
-O <sup>-</sup>	oxido	O <sup>2-</sup>	oxide
-O <sub>2</sub> <sup>-</sup>	peroxido	O <sub>2</sub>	dioxygen
-PO <sub>3</sub> <sup>2-</sup>	phosphonato		
-NH <sub>3</sub> <sup>+</sup>	ammonio	NH <sub>3</sub>	ammonia
-N <sub>2</sub> <sup>+</sup>	diazonio	N <sub>2</sub>	dinitrogen
-OH <sub>2</sub> <sup>+</sup>	oxonio	H <sub>2</sub> O	water

TABLE 3. An illustrative list of names of multivalent groups and of groups with more than one univalent point of attachment, and of related entities of specified oxidation level.

-CH <sub>2</sub>	methylidene	-CHCH <sub>3</sub>	ethylidene
-NH	imino	-NOH	hydroxyimino
-N <sub>2</sub>	diazo	=N	nitrilo
-O	oxo	-S	thioxo
-CH <sub>2</sub> <sup>-</sup>	methylene or methanediyl	-CH<	methanetriyl
>CH-CH <sub>3</sub>	ethane-1,1-diyl	-CH <sub>2</sub> CH <sub>2</sub> <sup>-</sup>	ethylene
-NH-	aminediyl or imino		
-O-O-	peroxy or dioxidanediyl	-S-	sulfanediyil or thio
CH <sub>2</sub>	methylene or carbene	CR <sub>2</sub>	carbene (generic)
NH	aminylene or nitrene	NR	nitrene (generic)
O <sub>2</sub>	dioxygen	S	sulfur

TABLE 4. An illustrative list of names of silicon and phosphorus groups.

-SiMe <sub>3</sub>	trimethylsilyl	-O-SiMe <sub>3</sub>	trimethylsilyloxy or trimethylsiloxy
-SiMe <sub>2</sub> <sup>-</sup>	dimethylsilanediyl	-SiH <sub>2</sub> OSiH <sub>2</sub> <sup>-</sup>	disiloxane-1,3-diyl
-PH <sub>2</sub>	phosphanyl or phosphino	-PH <sub>4</sub>	λ <sup>5</sup> -phosphanyl or phosphoranyl
-P(O)Me <sub>2</sub>	dimethylphosphinoyl	-O-PMe <sub>2</sub>	dimethylphosphanyloxy
-P(O)(OH) <sub>2</sub>	phosphono	-PO <sub>3</sub> <sup>2-</sup>	phosphonato

## 0 GENERAL RULES APPLICABLE TO THE NAMES OF ALL TRANSFORMATIONS

**0.1 Construction of names.** In general the names for a transformation describe the conversion of substrate into product by listing the names of groups that become attached to the substrate or detached from it or that migrate from one site to another, and by the use of positional locants and of words and/or syllables that give information about the nature of primitive changes (defined in reference 2) occurring within the transformation and about the class of the transformation.

**0.1.1** If there is more than one group within any one of the categories of attaching, detaching, or migrating groups, their names are separated by commas. The major components of the name, that is, the different strings of group names, their positional locants, and informative words and syllables, are separated by hyphens. Exceptionally: (a) neither a hyphen nor a comma is used after a post-slash arabic numeral (Rule 0.3), and (b) in simple speech/writing names hyphens may be omitted if clarity is not thereby diminished.

**0.1.2** The name of any complex group or entity may be enclosed in square brackets for clarification.

**0.1.3** In a transformation in which groups or entities are both attached to and detached from the substrate, those that are attached are listed first, followed by the syllable “-de-”, followed by those that are detached.

**0.2 Priority.** When more than one group or entity is present in a string, the order is defined by two criteria: (a) groups or entities are listed in order of increasing valence (in this context, “valence” means the number of formal covalent bonds to that group or entity from the rest of the molecule); (b) groups or entities of the same valence are listed in order of increasing priority as defined (for univalent groups or entities) by the Cahn-Ingold-Prelog rules<sup>4</sup> or (for groups or entities of higher valence) by the principles of those rules.

**Examples:**

- 1 hydroxy (-OH) is listed before oxo (=O)
- 2 carboxy (-COOH) is listed before fluoro (-F)
- 3 1-fluoroethyl (-CHFCH<sub>3</sub>) is listed before 1-chloroethyl (-CHClCH<sub>3</sub>)
- 4 hydroxymethyl (-CH<sub>2</sub>OH) is listed before formyl (-CHO)
- 5 formyl (-CHO) is listed before dimethoxymethyl (-CH(OCH<sub>3</sub>)<sub>2</sub>)
- 6 phenylimino (=NPh) is listed before oxo (=O)

**0.2.1** When groups or entities are named generically their priority is that of the lowest-priority member of the genus.

**Examples:**

- 1 The priority of the genus “halogen” is defined by that of fluorine.
- 2 The priority of the genus “alkoxy” is defined by that of methoxy.

**0.3 Site designation.** In transformations that entail connectivity changes at more than one site of the substrate the relative positions of substrate atoms are denoted by post-slash arabic numerals, numbered consecutively from the prime site which is designated 1/. Unless specifically ruled otherwise, the prime site is selected by applying the following criteria in order.

- (a) A site from which detachment occurs is numbered 1/ in preference to a site to which attachment occurs.
- (b) The prime site is selected so that as low a number as possible appears at the first point in the name of a transformation at which the assigned numbers would differ.
- (c) The prime site is selected so that at the first point of difference the lower number is associated with a substrate atom of higher atomic number.

**Examples:**

- 1 Criterion (a). In allylic substitutions (Rule 1.4) the site of the leaving group is designated 1/.
- 2 Criterion (b). In perhydroaddition to EtCH=CHC=N (Example 1 under Rule 2.2.2.4), it is the nitrogen atom that is designated 1/, giving the numbering sequence 1/1/2/2/3/4/. If the  $\beta$  carbon atom were the prime site, the sequence would be 1/2/3/3/4/4/. However, in perhydroaddition to EtC=CCH=NH the  $\beta$  carbon atom is designated 1/ and the nitrogen is 4/.
- 3 Criterion (c). In perhydroaddition to CH<sub>2</sub>=C=O (to give CH<sub>3</sub>-CH<sub>2</sub>-OH), it is the oxygen atom that is designated 1/ rather than the methylene carbon atom.

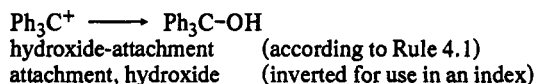
In some speech/writing names it may be permissible to omit site designations: such occasions are referred to specifically in subsequent rules.

**0.3.1** When one or more of the reacting sites of the substrate is an element other than carbon, then all the reacting sites are designated by italicised atomic symbols. Unless specifically ruled otherwise, these symbols are located as follows: (a) if connectivity changes occur only at one site of the substrate, then the symbol is placed at the start of the name; (b) if connectivity changes involve the cleavage or formation of a bond between two sites of the substrate, as in insertion and extrusion transformations and ring opening and closing transformations, the symbols for the atoms at each end of the bond are placed at the start of the name; (c) otherwise the symbol is placed immediately after the post-slash arabic numeral denoting the position of the site.

In speech/writing names the atomic symbol *C* may be omitted if ambiguity does not ensue. In simple transformations in which the context makes their nature obvious, it may be permissible to omit all atomic symbols: such occasions are referred to specifically in subsequent rules.

**0.4 Inversion of names for indexing.** Any transformation name may be inverted for the purposes of indexing, placing the term that characterises the type of transformation at the front of the name.

**Example:**



## 1 SUBSTITUTION TRANSFORMATIONS

**1.1 Univalent-univalent substitutions.** These are transformations in which a univalent atom or group is replaced at the same site by another univalent atom or group.

**1.1.1** For speech/writing, the name comprises (a) the name of the entering group, (b) the syllable “-de-”, (c) the name of the leaving group, and (d) the suffix “ation”. For euphony or to accord with traditional usage, slight changes in spelling may be made at the end of the name of the leaving group.

**1.1.2** For indexing, the name comprises (a) the name of the entering group, (b) the syllable “-de-”, (c) the name of the leaving group, and (d) the suffix “-substitution”.

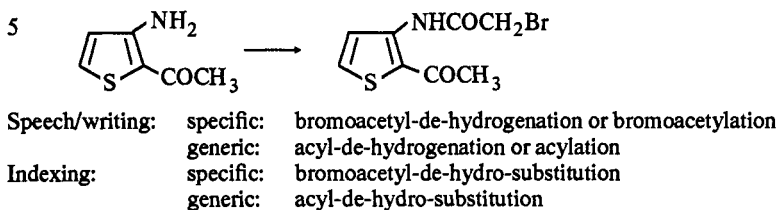
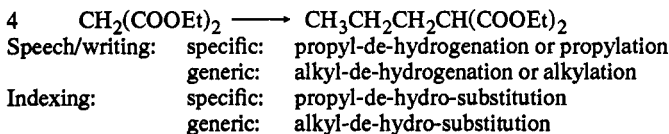
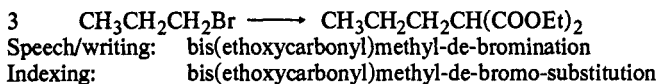
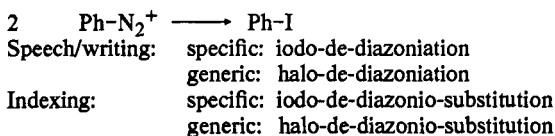
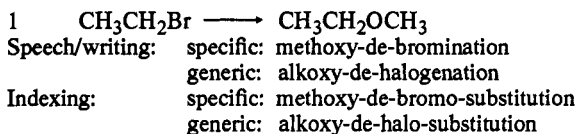
(Attention is called to the difference in the endings between speech/writing and indexing names for substitutions. Justification for this difference stems in part from general considerations stated in the Preamble, in part from the fact that the “ation” suffix for substitution names has been in use since 1954, and in part from the utility of the suffix “substitution” in indexing names in their inverted form (Rule 0.4). Indexing names may be used in speech or writing if one wishes to do so.)

**1.1.3 Introduction or replacement of hydrogen.** Hydrogen of natural or unspecified isotopic abundance is represented as “hydro”, except that when a leaving group it is represented as “hydrogen” in speech/writing names. (See examples 4, 5, 6 and 7.) When a distinction is made between isotopes of hydrogen  $^1\text{H}$  is represented as “protio”,  $^2\text{H}$  as “deuterio” and  $^3\text{H}$  as “tritio”. (See example 6.)

For speech/writing, specific mention of hydrogen as an entering or leaving group may optionally be omitted. If hydrogen is the entering group, the name then comprises (a) the syllable “de”, (b) the name of the leaving group, and (c) the suffix “ation”. (Example 7.) If hydrogen is the leaving group, the name comprises (a) the name of the entering group and (b) the suffix “ation”. (Examples 4, 5, and 6.) In either case, for euphony slight changes in spelling may be made at the end of the name of the group. In this usage it would be normal to omit hyphens before or after “de”.

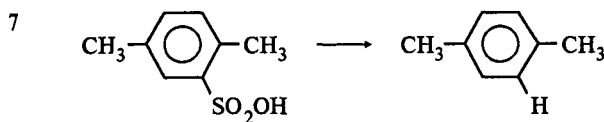
**1.1.4 Naming of groups.** Leaving groups are named as they are in the substrate; entering groups as they are in the product.

**Examples:**

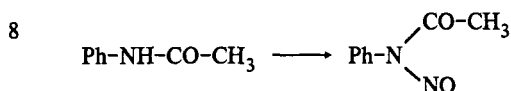




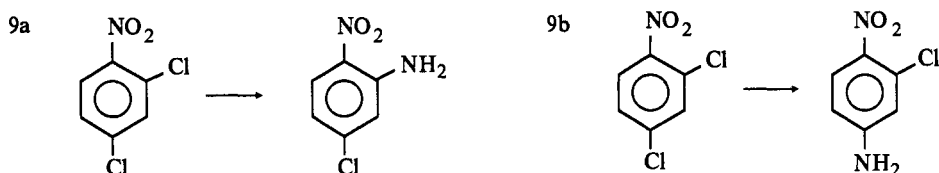
- 6  $C_6H_6 \longrightarrow C_6H_5NO_2$   
 Speech/writing: nitro-de-hydrogenation or nitration  
 Indexing: nitro-de-hydro-substitution  
 If it is desired to distinguish among hydrogen isotopes, the following names could be used.  
 Speech/writing: nitro-de-protiation, nitro-de-deuteriation, nitro-de-tritiation  
 Indexing: nitro-de-protio-substitution, etc.



- Speech/writing: hydro-de-sulfonation or desulfonation  
 Indexing: hydro-de-sulfo-substitution



- Speech/writing: *N*-nitroso-de-hydrogenation or *N*-nitrosation  
 Indexing: *N*-nitroso-de-hydro-substitution



Both processes are examples of the same transformation, namely:

- Speech/writing: amino-de-chlorination  
 Indexing: amino-de-chloro-substitution

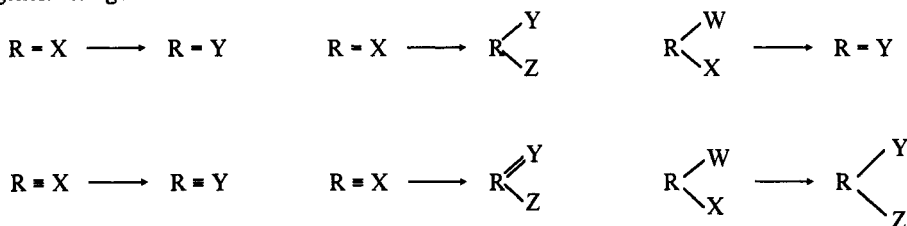
However, in casual usage in speech or writing (see section 5, "Site Designation", in the Preamble) one may wish to make a distinction between the two by saying:

- for 9a: 2-amino-dechlorination  
 for 9b: 4-amino-dechlorination } of 2,4-dichloronitrobenzene

- 10 (*R*)-*sec*-butyl bromide  $\longrightarrow$  (*S*)-*sec*-butyl ethyl sulfide  
 The transformation is ethylthio-de-bromination (for speech/writing) or ethylthio-de-bromo-substitution (for indexing). Either may be followed by "(with inversion of configuration)".

- 11  $PhI \xrightarrow{((EtO)_2PO^-Na^+)} Ph-PO(OEt)_2$   
 The transformation is diethoxyphosphinoyl-de-iodination (for speech/writing) or diethoxyphosphinoyl-de-iodo-substitution (for indexing). A chemist might wish to convey more information as well as an opinion about mechanism by stating that it is photo-induced diethoxyphosphinoyl-de-iodination (probably by the  $S_{RN}1$  mechanism).

**1.2 Multivalent-multivalent substitutions.** These are transformations involving the replacement at the same site of a multivalent atom or group and/or of more than one atom or group. For example, they include the following general categories:



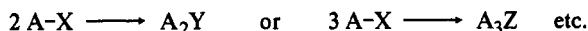
The "multiplicity" of such a transformation is defined as the number of formal covalent bonds from the substrate that are broken or made. Note that this rule embraces transformations (such as the hydrolysis of a nitrile to a carboxylic acid) which are not mechanistically simple substitutions.

Except for the usage described in Rule 1.2.2, simultaneous substitutions at two or more different sites are regarded as separate transformations; each must be named separately.



- 12  $\text{CH}_3\text{CN} \longrightarrow \text{CH}_3\text{COOH}$   
hydroxy,oxo-de-nitrilo-tersubstitution
- 13  $\text{CSCl}_2 \longrightarrow \text{CO}_2$   
Specific: dioxo-de-dichloro,thioxo-quatersubstitution  
Generic: dioxo-de-dihalo,thioxo-quatersubstitution
- 14  $\text{SbCl}_5 \xrightarrow{(\text{MeMgI})} \text{SbMe}_5$   
Specific: *Sb*-pentamethyl-de-pentachloro-quinquesubstitution  
Generic: *Sb*-pentaalkyl-de-pentahalo-quinquesubstitution
- 15  $\text{PhSF}_5 \longrightarrow \text{PhSO}_2\text{OH}$   
Specific: *S*-hydroxy,dioxo-de-pentafluoro-quinquesubstitution  
Generic: *S*-hydroxy,dioxo-de-pentahalo-quinquesubstitution

**1.3 "Aggregating" substitutions.** These are transformations in which an identical leaving group from each of two or more identical substrate entities is replaced by a single multivalent incoming group to form a product in which the remaining parts of the substrate entities are all equivalent; that is, they are transformations of the type:



These transformations could be named by Rule 1.1 as "AY-de-X-substitutions" or "A<sub>2</sub>Z-de-X-substitutions", but such names disguise the symmetry of the transformation. To emphasise this the "aggregating" nomenclature described below is used. (Compare also the discussion of coupling and uncoupling transformations, Rule 6.1.)

**1.3.1** The name of an "aggregating" substitution comprises: (a) the name of the entering group, (b) the syllable "-de-", (c) the name of the leaving group preceded by the appropriate multiplier for the number of substrate entities (di-, tri-, tetra-), (d) the suffix "aggre-substitution".


**Examples:**

- 1  $2 \text{C}_2\text{H}_5\text{OH} \longrightarrow (\text{C}_2\text{H}_5\text{O})_2\text{CH}_2$   
*O*-methylene-de-dihydro-aggre-substitution
- 2  $2 \text{C}_6\text{H}_5\text{I} \longrightarrow \text{C}_6\text{H}_5\text{-CH}_2\text{-CH}_2\text{-C}_6\text{H}_5$   
ethylene-de-diiodo-aggre-substitution
- 3  $2 \text{CH}_3\text{Br} \longrightarrow \text{CH}_3\text{-O-O-CH}_3$   
peroxy-de-dibromo-aggre-substitution
- 4  $2 \text{ArH} \longrightarrow \text{Ar-S-Ar}$   
thio-de-dihydro-aggre-substitution
- 5  $3 \text{CH}_3\text{OH} \longrightarrow (\text{CH}_3\text{O})_3\text{CCH}_3$   
*O*-ethanilydyne-de-trihydro-aggre-substitution
- 6  $4 \text{PhSH} \longrightarrow (\text{PhS})_4\text{C}$   
*S*-methanetetrayl-de-tetrahydro-aggre-substitution

**1.4 Allylic and related substitutions.** These are substitution transformations in which the incoming group becomes attached to a site different from that which bore the leaving group, but in which there is no other change of connectivity in the substrate. This rule does not, therefore, include transformations such as the cine-substitution of a halogenobenzene, which is covered in Rule 5.

These transformations are named according to Rules 1.1 and 1.2, with the addition of a post-slashed arabic numeral to indicate the site of the incoming group relative to that of the leaving group, which is taken implicitly as 1/.

**Examples:**

- 1  $\text{CH}_2=\text{CH-CHMe-Br} \longrightarrow \text{HO-CH}_2\text{-CH-CHMe}$   
Speech/writing: 3/hydroxy-de-bromination  
Indexing: 3/hydroxy-de-bromo-substitution
- 2  $\text{CH}_2=\text{CH-O-CMe}_3 \longrightarrow \text{CH}_3\text{-CH-O}$   
Speech/writing: 3/hydro-de-*O*-*tert*-butylation  
Indexing: 3/*C*-hydro-de-*O*-*tert*-butyl-substitution
- 3   
Speech/writing: 5/chloro-de-bromination  
Indexing: 5/chloro-de-bromo-substitution

## 2 ADDITION TRANSFORMATIONS

**2.1 Addition of two univalent groups.** These rules deal with transformations as a result of which two univalent atoms or groups (called addends) become attached to an unsaturated substrate. These transformations include addition to simple olefins, to carbonyl groups, to aldimines and ketimines, to dienes, to aromatic or heteroaromatic substrates, to acetylenes, to carbenes and nitrenes, to 1/3/dipolar intermediates, and others of similar kind.

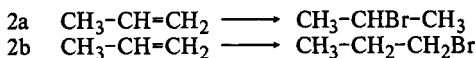
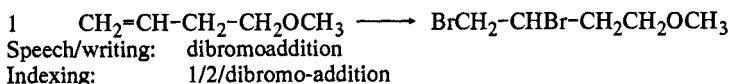
### 2.1.1 Addition to a single olefinic or acetylenic linkage.

**2.1.1.1** The indexing name comprises (a) the locant 1/ and the name of the addend of lower priority as defined in Rule 0.2, (b) the locant 2/ and the name of the addend of higher priority, and (c) the suffix “-addition”. Groups are named according to Rule 1.1.4. (See examples 2, 3, 6, 7 and 8.)

**2.1.1.2** If the two addends are the same, the name comprises (a) the locants 1/2/, (b) the syllable “di” or “bis” (as appropriate <sup>6</sup>), (c) the name of the addend, and (d) the suffix “-addition”. (See examples 1 and 4.)

**2.1.1.3** In speech/writing names the locants 1/, 2/ and the hyphens may be omitted.

#### Examples:

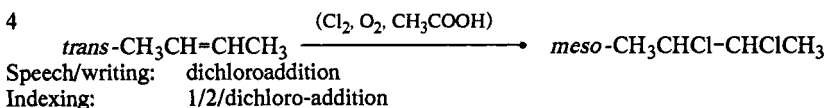
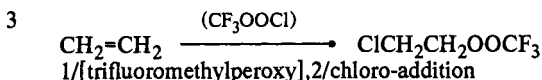


Both transformations are:

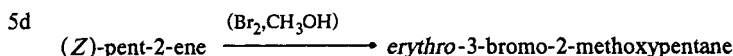
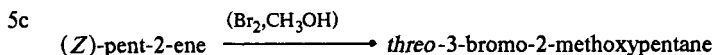
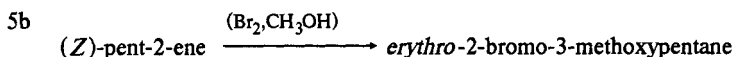
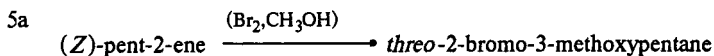
Speech/writing: hydro,bromo-addition  
 Indexing: 1/hydro,2/bromo-addition

In casual use in speech and writing (compare section 5, “Site Designation”, in the Preamble) one may wish to make a distinction between the two by saying:

for 2a: 1-hydro-2-bromoaddition  
 for 2b: 2-hydro-1-bromoaddition } to propene



One could introduce a parenthetic description of stereochemistry (see section 6, “Mechanistic Information”, in the Preamble) by writing: (*anti*)1/2/dichloro-addition.



All these processes are examples of a single transformation, namely:

Specific: methoxy-bromo-addition or 1/methoxy-2/bromo-addition

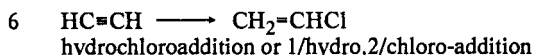
Generic: alkoxy,halo-addition or 1/alkoxy,2/halo-addition.

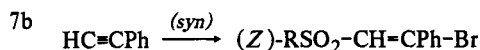
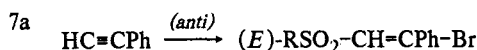
In casual usage additional information could be given as in the following examples:

For 5a and 5c: (*anti*)1/methoxy,2/bromo-addition

For 5a and 5b: 3-methoxy,2-bromo-addition to (*Z*)-pent-2-ene

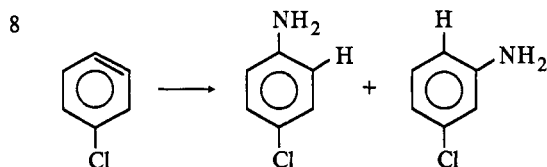
For 5d: (*syn*)2-methoxy,3-bromo-addition to (*Z*)-pent-2-ene





For 7a: (*anti*)alkylsulfonyl,bromo-addition or (*anti*)1/alkylsulfonyl,2/bromo-addition

For 7b: (*syn*)alkylsulfonyl,bromo-addition or (*syn*)1/alkylsulfonyl,2/bromo-addition

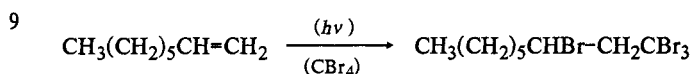


Both transformations are examples of:

hydro-amino-addition or 1/hydro-2/amino-addition

In casual use in speech and writing a distinction may be made by saying:

2-hydro,1-amino-addition or  
1-hydro,2-amino-addition } to 4-chlorobenzene



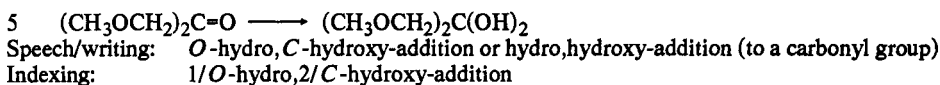
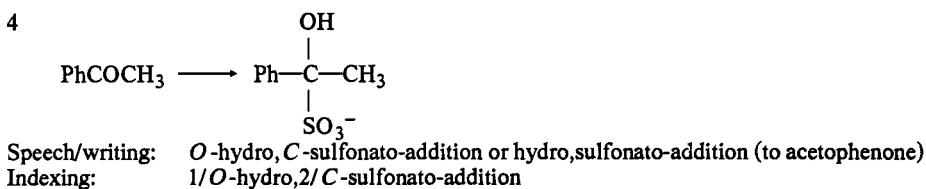
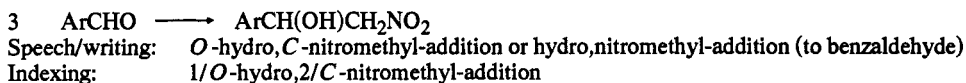
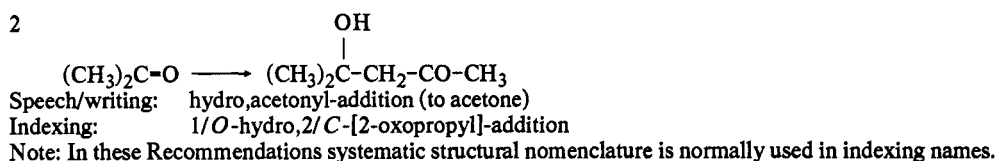
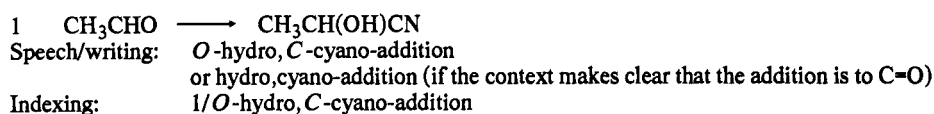
1/[tribromomethyl],2/bromo-addition

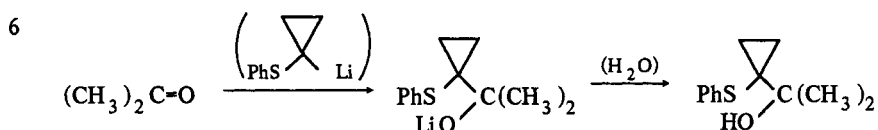
In casual usage (compare section 5, "Site Designation", in the Preamble) one could describe the process as photoinitiated 1-[tribromomethyl],2-bromo-addition of CBr<sub>4</sub> to oct-1-ene by a radical mechanism.

**2.1.2 Addition to multiple bonds involving heteroatoms.** Names are formulated as under Rule 2.1.1 save that the names of the addends are preceded by italicised atomic symbols of the sites of addition. If the addends are identical the substrate sites are numbered in order of decreasing atomic number. (Rule 0.3; see example 7.)

In speech/writing names atomic symbols may be omitted if the context makes clear the nature of the transformation.

**Examples:**





For transformation of acetone to intermediate:

Speech/writing: generic: metallo,alkyl-addition (to acetone)  
 Indexing: generic: 1/O-metallo,2/C-alkyl-addition  
 specific: 1/O-lithio, 2/C-[1-(phenylthio)cyclopropyl]-addition

For transformation of intermediate to final product (Rule 1.1):

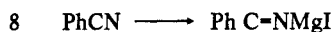
Speech/writing: generic: O-hydro-de-metallation  
 specific: O-hydro-de-lithiation  
 Indexing: generic: O-hydro-de-metallo-substitution  
 specific: O-hydro-de-lithio-substitution

For transformation of acetone to final product:

Speech/writing: generic: hydro,alkyl-addition (to acetone)  
 Indexing: generic: 1/O-hydro,2/C-alkyl-addition  
 specific: 1/O-hydro, 2/C-[1-(phenylthio)cyclopropyl]-addition



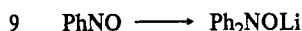
Speech/writing: O,C-dihydro-addition or dihydroaddition (to acetaldehyde)  
 Indexing: 1/O,2/C-dihydro-addition



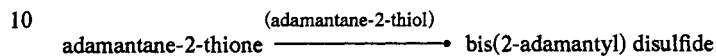
|  
CH<sub>3</sub>

Speech/writing: specific: C-methyl,N-iodomagnesio-addition  
 or methyl,iodomagnesio-addition (to benzonitrile)  
 generic: N-metallo,C-alkyl-addition  
 Indexing: specific: 1/C-methyl,2/N-iodomagnesio-addition  
 generic: 1/N-metallo,2/C-alkyl-addition

Note that the Rule for designating the priorities of generic names (0.2.1) results in a difference between the specific and generic names in the order of listing the addends according to Rule 2.1.1.1. Such anomalies are uncommon but, occasionally, unavoidable. In Example 9 specific and generic priorities are the same.



Speech/writing: specific: O-lithio,N-phenyl-addition  
 generic: O-metallo,N-aryl-addition  
 Indexing: specific: 1/O-lithio,2/N-phenyl-addition  
 generic: 1/O-metallo,2/N-aryl-addition

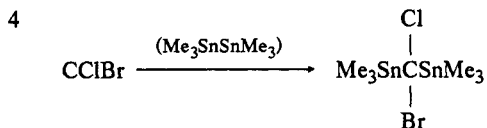
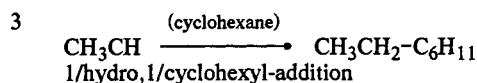
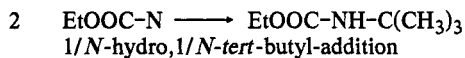
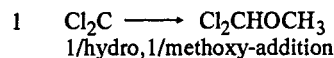


Speech/writing: generic: C-hydro,S-alkylthio-addition  
 Note that it is not desirable to omit atomic symbols, because they distinguish this transformation from the formation of a dithiohemiacetal.

Indexing: specific: 1/C-hydro,2/S-[2-adamantylthio]-addition  
 generic: 1/C-hydro,2/S-alkylthio-addition

**2.1.3 Addition to a carbene or a nitrene.** The rules are the same as for addition to a single olefinic linkage, except that for speech/writing it is usually desirable to emphasize the character of the transformation by including the locants "1'", "1'" and, for nitrenes, the atomic symbols. (For indexing they are requisite.)

**Examples:**

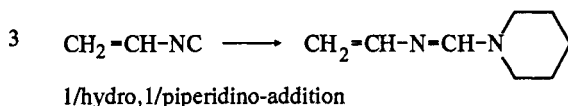
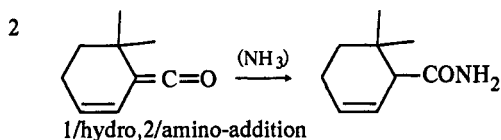
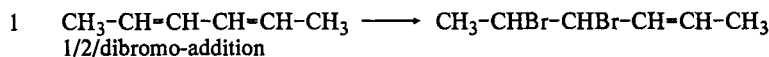


specific: 1/1/bis(trimethylstannyl)-addition  
 generic: 1/1/distannyl-addition

### 2.1.4 Addition to conjugated, cumulative or other extended unsaturated substrates.

2.1.4.1 If addition occurs only across two adjacent atoms or to a single centre (e.g. a carbene or nitrene), then Rules 2.1.1 to 2.1.3 apply: the remainder of the unsaturated substrate is irrelevant to the name of the transformation.

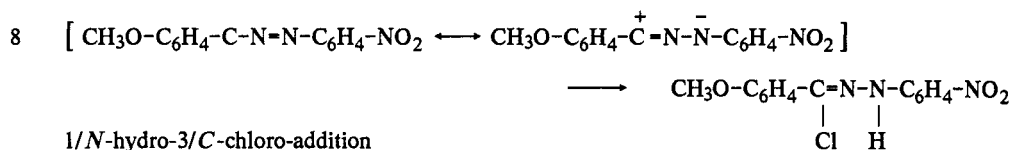
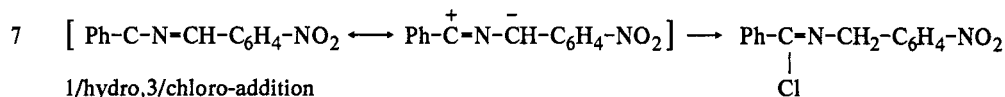
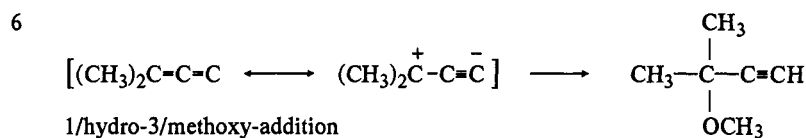
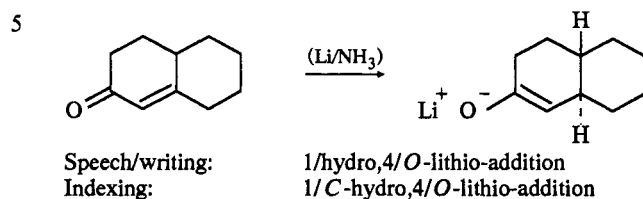
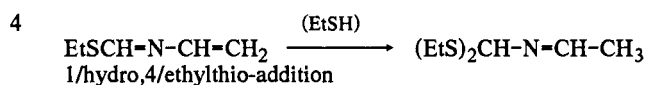
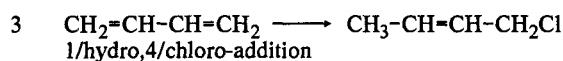
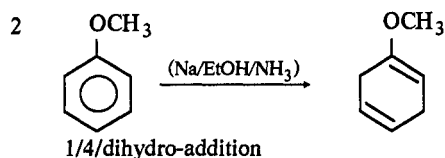
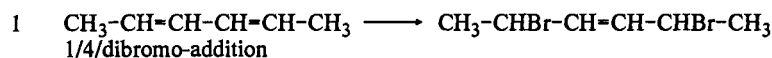
**Examples:**



2.1.4.2 When the addends attach to sites that are separated by one or more atoms, then that part of the unsaturated substrate that undergoes addition is numbered consecutively with post-slashed arabic numerals, atom 1/ being the site to which the first-named addend is attached (Rule 0.3). With this modification, Rules 2.1.1 to 2.1.3 are then applied. (Rule 2.1.1.3 is not applicable.) Changes in the location of  $\pi$ -bonds are not specifically described in the name of the transformation.

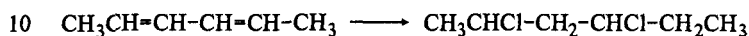
It is usually undesirable to omit the atomic symbol for a heteroatom, but the symbol *C* may be omitted in speech/writing names if no ambiguity ensues. (See Example 5.)

**Examples:**





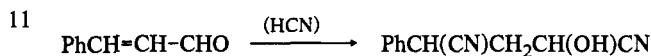




Indexing or speech/writing: 1/3/dihydro,2/4/dichloro-biaddition

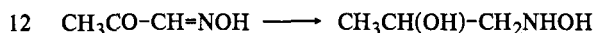
Speech/writing only\*: bis-(hydro,chloro-addition)

[\* Rule 2.2.1.2]



Speech/writing: 1/O,3/dihydro,2/4/dicyano-biaddition

Indexing: 1/O,3/C-dihydro,2/C,4/C-dicyano-biaddition



Speech/writing or indexing: 1/O,2/C,3/C,4/N-tetrahydro-biaddition

Note: The letter *C* is used differently in examples 11 and 12. When only the 1/ atom is not carbon there is little ambiguity in omitting *C*. In the present example, however, "2/3/4/N" could be thought to imply that atoms 2/ and 3/ were nitrogen.

**2.2.2 Additions of multiplicity greater than two** are named by analogy with the Rule (2.2.1) for biadditions with appropriate changes to the numerical prefixes. Additions of multiplicity three, four, five, etc, are named teradditions, quateradditions, quinquadditions, etc, respectively.

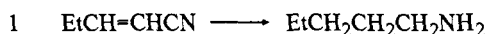
**2.2.2.1** Post-slashed arabic locants should always be used, except as laid down in Rule 2.2.2.3.

**2.2.2.2** If the atom designated 1/ is the only heteroatom in the unsaturated substrate, then for speech/writing the symbol *C* for the other atoms may be omitted. (See examples 1 and 3.)

**2.2.2.3** If, in an addition with multiplicity greater than two, all the addends are identical and the product of addition is fully saturated, then in speech/writing the transformation may optionally be named using (a) the prefix "per", (b) the name of the addend followed by a hyphen, and (c) the suffix "addition". (Example 1.)

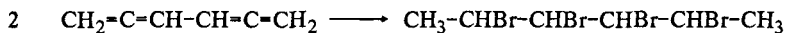
**2.2.2.4** The usage described in Rule 2.2.1.2 may be extended to more than two non-cumulative double bonds by using the appropriate multiplying prefix, "*tris-*", "*tetrakis-*", etc.

#### Examples:

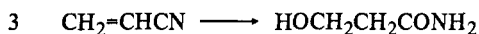


Speech/writing: 1/1/N,2/2/3/4/hexahydro-teraddition or perhydroaddition

Indexing: 1/1/N,2/2/C,3/C,4/C-hexahydro-teraddition

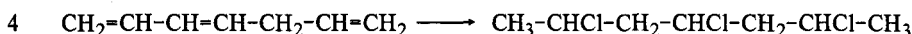


Speech/writing or indexing: 1/2/5/6/tetrahydro,2/3/4/5/tetrabromo-quateraddition



Speech/writing: 1/1/N,3/trihydro,4/hydroxy,2/oxo-teraddition

Indexing: 1/1/N,3/C-trihydro,4/C-hydroxy,2/C-oxo-teraddition



For indexing this must be named as two separate transformations (a biaddition and a monoaddition). For speech/writing it would be permissible, applying Rule 2.2.2.4, (but not obligatory) to name it as: *tris*-(hydro,chloro-addition)

## 3 ELIMINATION TRANSFORMATIONS

**3.1 Elimination of two univalent groups.** These rules deal with transformations in which two univalent atoms or groups (called eliminands) are detached geminally (to form a carbene, nitrene, etc.), vicinally (to form an olefin, a carbonyl group, an imine, etc.), from positions which are separated by one atom (to form certain reactive intermediates), or from positions separated by more than one atom (e.g., to form a conjugated diene). Elimination from two vicinal positions joined by a double bond (to form a triple bond between those positions) is embraced. Detachment of atoms or groups from positions separated by methylene groups, ether bridges and the like, accompanied by bonding of those positions to each other so as to form a ring structure of three or more ring members, is excluded.

(Note. During the development of these rules, names such as "dehydrobromination" (which has appeared to some extent in the literature) and "de-hydro-de-bromination" were considered but were rejected because to the ear and even to the eye they closely resemble "hydro-de-bromination" which represents a substitution transformation. The usage that has been adopted, "hydro,bromo-elimination", is distinctive and self-explanatory.)

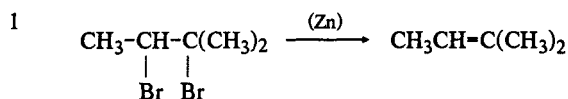
**3.1.1 Elimination to form a single olefinic or acetylenic linkage.**

**3.1.1.1** The name comprises (a) the locant 1/ and the name of the eliminand of lower priority as defined in Rule 0.2, (b) the locant 2/ and the name of the eliminand of higher priority, and (c) the suffix "-elimination". Groups are named according to Rule 1.1.4.

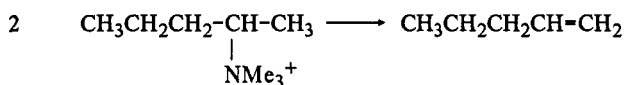
3.1.1.2 If the two eliminands are the same, the name comprises (a) the locants 1/2/, (b) the syllable “di” or “bis” (as appropriate; see ref. 6), (c) the name of the eliminand and (d) the suffix “-elimination”.

3.1.1.3 In speech/writing names the locants 1/ and 2/ and the hyphens may be omitted.

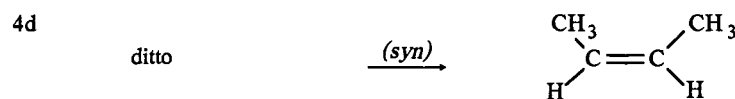
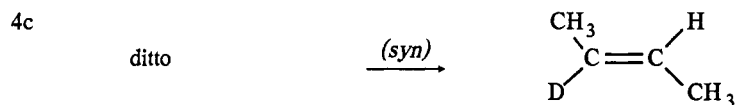
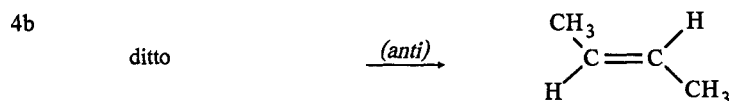
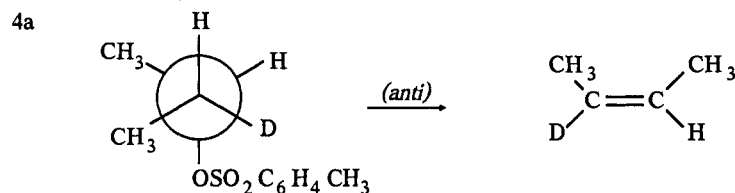
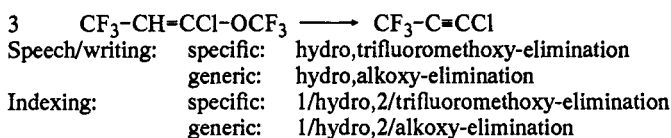
**Examples:**



Speech/writing: dibromoelimination  
Indexing: 1/2/dibromo-elimination



Speech/writing: hydro,[trimethylammonio]-elimination  
Indexing: 1/hydro,2/[trimethylammonio]-elimination

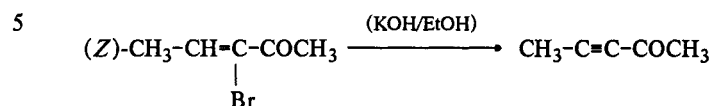


4a - 4d are all examples of the same transformation, namely:

Speech/writing: hydro,[*p*-tolylsulfonyloxy]-elimination  
Indexing: 1/hydro,2/[*p*-tolylsulfonyloxy]-elimination

Variations on the name include:

For 4a and 4c: 1/protio,2/[*p*-tolylsulfonyloxy]-elimination  
For 4b and 4d: 1/deuterio,2/[*p*-tolylsulfonyloxy]-elimination  
For 4a: (*anti*)-protio,[*p*-tolylsulfonyloxy]-elimination

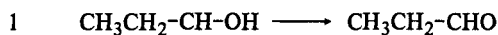


Speech/writing: hydro,bromo-elimination or  
(*anti*)-hydro,bromo-elimination  
Indexing: 1/hydro,2/bromo-elimination

### 3.1.2 Elimination to form a multiple bond between carbon and an atom of another element.

Names are formulated as for elimination to form single olefinic linkages, except that names of the eliminands are preceded by the italicised atomic symbols of the sites of elimination. When the eliminands are identical the substrate sites are numbered in order of decreasing atomic number (Rule 0.3; see example 3). In speech/writing, this site designation may be omitted if the context makes clear the character of the transformation.

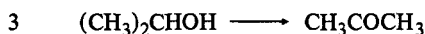
#### Examples:



Speech/writing: *O*-hydro-*C*-sulfonato-elimination  
Indexing: 1/*O*-hydro,2/*C*-sulfonato-elimination



Speech/writing: *C*-hydro,*O*-nitro-elimination  
Indexing: 1/*C*-hydro,2/*O*-nitro-elimination



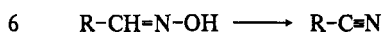
Speech/writing: *O*,*C*-dihydro-elimination  
or dihydroelimination (if the context indicates that a carbonyl group is formed)  
Indexing: 1/*O*,2/*C*-dihydro-elimination



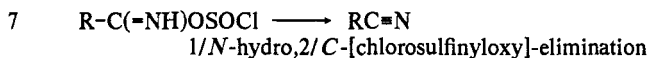
Speech/writing: *C*-hydro,*O*-dimethylsulfonio-elimination  
Indexing: 1/*C*-hydro,2/*O*-dimethylsulfonio-elimination



Speech/writing: *C*-hydro,*S*-cyano-elimination or hydro,cyano-elimination (to give a thione)  
Indexing: 1/*C*-hydro,2/*S*-cyano-elimination



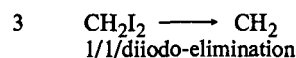
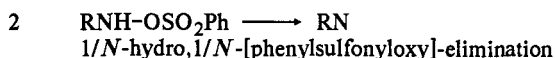
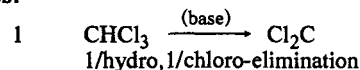
Speech/writing: *C*-hydro,*N*-hydroxy-elimination or hydro,hydroxy-elimination (from an oxime)  
Indexing: 1/*C*-hydro,2/*N*-hydroxy-elimination



Note: In a relatively complicated example such as this it may be preferable not to use simplified speech/writing names.

**3.1.3 Elimination to form a carbene or a nitrene.** The rules are the same as for elimination to form a single olefinic linkage except that for speech/writing usually desirable to emphasize the character of the transformation by including the locants "1/", "1/" and, for the formation of nitrenes, the atomic symbol. (For indexing they are requisite.)

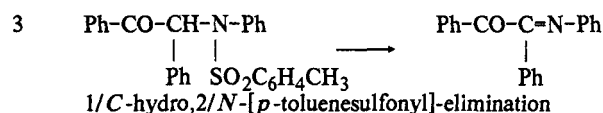
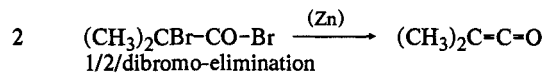
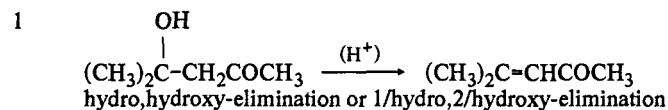
#### Examples:



### 3.1.4 Elimination to form a conjugated, cumulative or other extended unsaturated substrate.

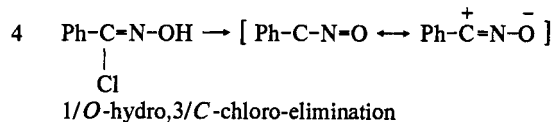
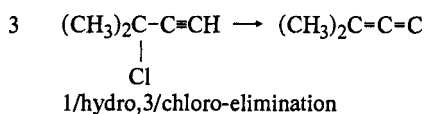
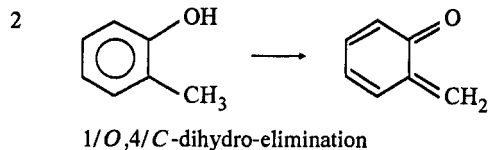
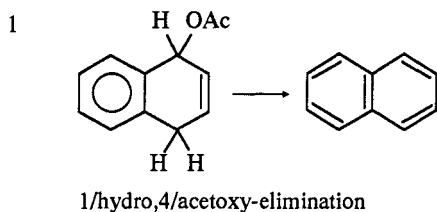
**3.1.4.1** If elimination occurs only from two adjacent atoms or from a single atom to form a carbene or nitrene, then Rules 3.1.1 to 3.1.3 apply: the remainder of the unsaturated system is irrelevant to the name of the transformation.

#### Examples:



3.1.4.2 When the eliminands detach from sites that are separated by one or more atoms, then that part of the substrate from which elimination occurs is numbered consecutively with post-slashed arabic numerals, atom 1/ being the site from which the first-named eliminand is detached. With this modification, Rules 3.1.1 to 3.1.3 are then applied. (Rule 3.1.1.3 is not applicable.) It is usually undesirable to omit atomic symbols for heteroatomic substrates, so that indexing and speech/writing names are identical.

**Examples:**



3.2 **Multivalent eliminations.** Rules under this heading deal with transformations in which multivalent eliminands or more than two univalent eliminands are detached to form a triple bond or a conjugated or cumulative unsaturated substrate. The multiplicity of these transformations is defined as one half of the combined valences of the eliminands. Except for the usage described in Rules 3.2.1.2 and 3.2.2.2, simultaneous eliminations which generate two or more isolated double bonds are regarded as separate transformations; each must be named separately.

The speech/writing names are the same as the indexing names unless otherwise stated.

3.2.1 **Eliminations of multiplicity two (bieliminations).** These are eliminations of four univalent eliminands, or of two divalent eliminands, or of one divalent and two univalent eliminands. The basic name comprises (a) the names of the eliminands in order of increasing valence, groups of the same valence being given in order of increasing priority as defined in Rule 0.2, each name being preceded by the appropriate site designation, and (b) the suffix “-bielimination”.

3.2.1.1 If the first-named eliminand (if divalent) or the first two (if univalent) detach from position 1/ and the remaining eliminand or eliminands detach from position 2/, then in the speech/writing names the positional numbers may optionally be omitted. In speech/writing the symbol *C* may be omitted if no ambiguity ensues.

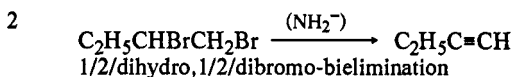
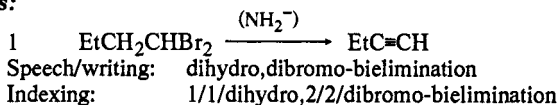
3.2.1.2 If a bielimination involves the elimination of two identical pairs of univalent eliminands to form two non-cumulative double bonds, each between an identical pair of atoms, then in speech/writing only it may be named by using the italicised prefix “*bis-*” followed in parentheses by the name of the corresponding monoelimination as described in Rule 3.1. This form of nomenclature may, if desired, be extended to include simultaneous eliminations which form isolated double bonds. (Compare Examples 3, 9.)

3.2.2 **Eliminations of multiplicity greater than two** are named by analogy with the Rule (3.2.1) for bieliminations with appropriate changes to the multiplying prefixes. Eliminations of multiplicity three, four, five, etc, are named tereliminations, quatereliminations, quinqueliminations, etc, respectively.

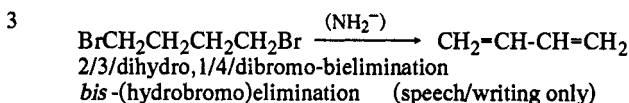
3.2.2.1 If the atom designated 1/ is the only heteroatom from which eliminands detach, then for speech/writing the symbol *C* for the other atoms may be omitted.

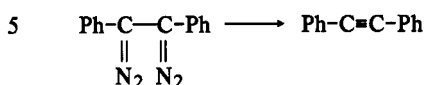
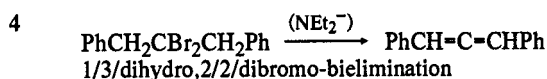
3.2.2.2 The usage described in Rule 3.2.1.2 may be extended to eliminations which form more than two non-cumulative double bonds by using the appropriate numerical prefix, “*tris-*”, “*tetrakis-*”, etc. (See example 9.)

**Examples:**



Note. The omission of locants is not desirable in writing (Rule 3.2.1.1), but in speech it may be permissible when it is obvious from the context what is meant.

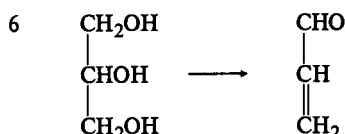




Speech/writing: bisdiazobielimination

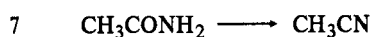
Indexing: 1/2/bisdiazobielimination

Note the use of "bis" (unitalicised, as in structural nomenclature) as a multiplier for a group whose name begins with a numerical prefix, in order to avoid "didiazo". This is distinct from italicised "bis-" as described in Rule 3.2.1.2 and illustrated in Example 3 above, to describe a multiple transformation.



Speech/writing: 1/0,2/dihydro,3/4/dihydroxy-bielimination

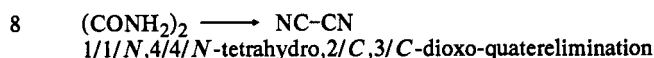
Indexing: 1/0,2/C-dihydro,3/C,4/C-dihydroxy-bielimination



Speech/writing: *NN*-dihydro, *C*-oxo-bielimination

Indexing: 1/1/*N*-dihydro,2/*C*-oxo-bielimination

Note: The optional omission of the letter *C* from the speech/writing name is not recommended in this example; the emphasis of *NN* at the beginning of the name needs to be counteracted.



For indexing this must be named as two separate transformations, a monoelimination plus a bielimination.

For speech/writing it is permissible, applying Rule 3.2.2.2, (but not obligatory) to name it as:

*tris*-(hydro,hydroxy-elimination)

#### 4 ATTACHMENT AND DETACHMENT TRANSFORMATIONS

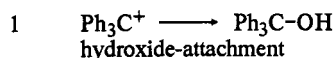
Attachment is a transformation under which the substrate is converted into another entity by the formation of one (and only one) two-centre bond (single or multiple) between the substrate and another entity, with no other changes in connectivity\* in the substrate. The origin of the entity that becomes attached to the substrate is not relevant to naming the transformation. Detachment is the reverse of attachment. In general the names of these transformations are the same for speech/writing as for indexing, but more specific alternatives to the name "attachment" (for example, "coordination" or "colligation") or "detachment" (for example, "heterolysis" or "homolysis") are permitted for speech/writing when they are consistent with common usage.

**4.1 Attachment transformations.** The name for these transformations comprises (a) the name of the entity that becomes attached to the substrate, followed by (b) the suffix "-attachment".

**4.1.1 Naming of entities attached.** The entity that becomes attached is named to balance the net charge encountered in the transformation. Thus, for transformations in which bromomethane is formed from the substrates  $\text{H}_3\text{C}^+$ ,  $\text{H}_3\text{C}^\cdot$ , and  $\text{H}_3\text{C}^-$ , the entities that become attached are bromide, bromine, and bromanylium, respectively, regardless of their origin.

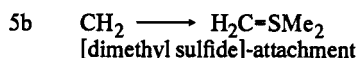
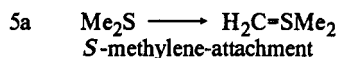
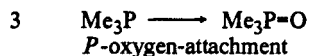
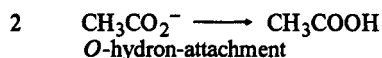
An entity may be named in a way that describes the site within it at which it becomes attached to the substrate, even though that is not the way in which the isolated entity would be named. Ambident ions and radicals may be named as if they had the particular structures that obtain in the product (compare Table 1 and examples 9 and 10) and parenthetical locants may be placed before the names of attaching entities to show the site of attachment (example 11b).

##### Examples:

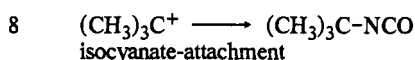
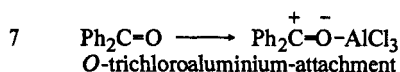
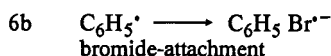
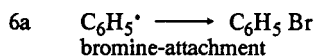


(Note that the transformation of  $\text{Ph}_3\text{C}^+$  to  $\text{Ph}_3\text{C}-\text{OH}$  is constant, though the reaction may be carried out in various ways, for example using  $\text{HO}^-$  or  $\text{H}_2\text{O}$  or  $\text{HOCO}_2^-$  as reagent.)

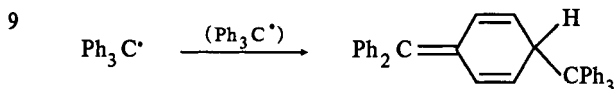
\* Note that connectivity is not related to bond order (reference 2, p. 1304). For example, in the attachment of  $\text{Br}^-$  to the allyl cation there are changes in the  $\pi$  bond order within the allyl moiety, but the only change in connectivity is the formation of the C-Br bond.



(Note that the reaction of  $\text{Me}_2\text{S}$  with  $\text{CH}_2$  can be named as two alternative attachment transformations. However, whereas  $\text{Me}_2\text{S} + \text{CH}_2\text{N}_2$  is an attachment if dimethyl sulfide is taken as the substrate, it is a *substitution* transformation of diazomethane.)



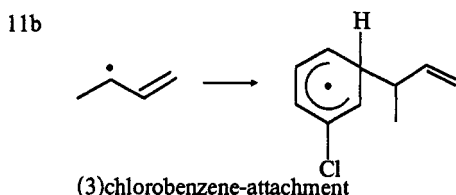
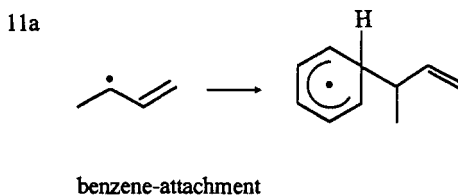
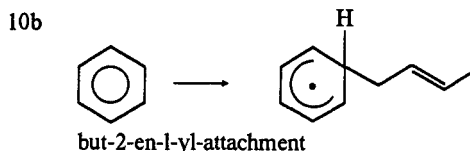
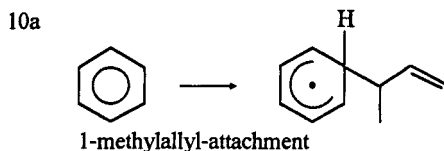
(Rule 4.1.1: "isocyanate" is used to signify attachment of the cyanate fragment via the nitrogen atom.)



There are two separate transformations in this example:

triphenylmethyl-attachment (to C-4' of the triphenylmethyl radical)

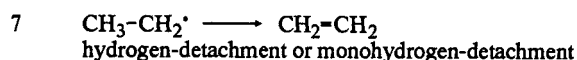
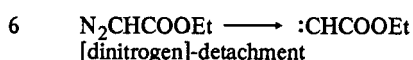
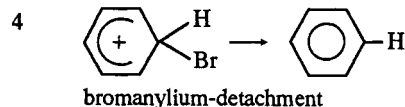
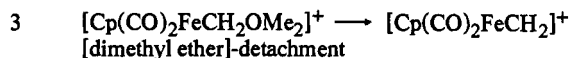
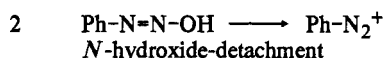
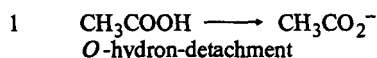
4-(diphenylmethylene)-cyclohexa-2,5-dienyl-attachment (to C-1 of the triphenylmethyl radical)



**4.2 Detachment Transformations.** The name for these transformations comprises (a) the name of the entity that becomes detached from the substrate, followed by (b) the suffix "-detachment".

**4.2.1 Naming of Entities Detached.** The entity that has been detached is named to balance the net charge encountered in the transformation (compare Rule 4.1.1).

**Examples:**



## 5 SIMPLE REARRANGEMENT TRANSFORMATIONS

### 5.1 Scope of the rule

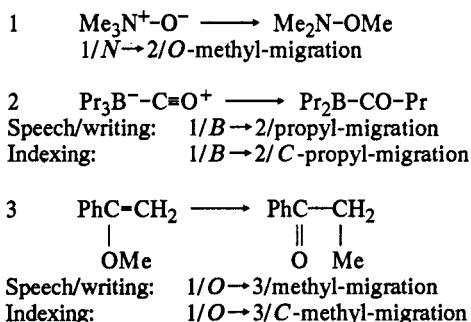
The transformations named by these rules are those in which a group changes its point of attachment, whether or not accompanied by any other transformation. Allylic rearrangements are not included: they are covered by Rule 1.4. Rearrangements associated with ring opening or closing are treated under Rule 8. More complex rearrangements appear in the list of complex transformations appended to these Rules.

In none of the transformations named by this rule are changes in the location of  $\pi$ -bonds specifically described in the name of the transformation.

### 5.2 Migrations unaccompanied by any other transformations.

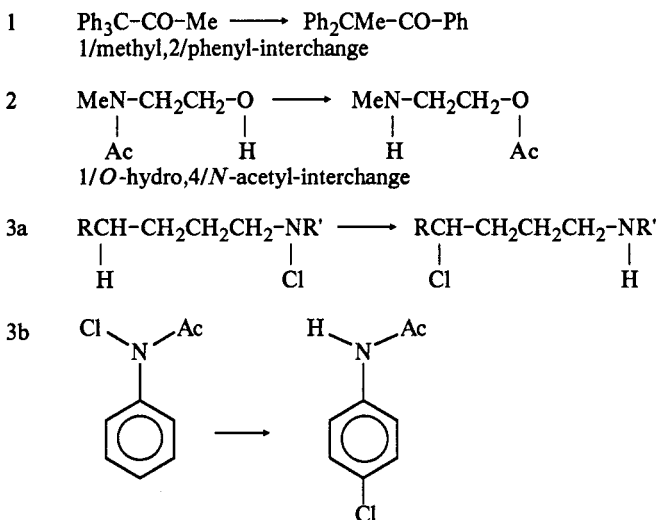
**5.2.1 Single migrations.** The name comprises: (a) the site designations for the site from which the migrating group departs (which is given the locant 1/) and that to which it moves, separated by an arrow ( $\rightarrow$ ), (b) the name of the migrating group, and (c) the suffix "-migration". In speech the arrow symbol is pronounced "to".

**Examples:**



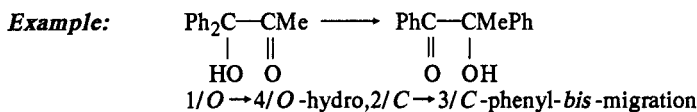
**5.2.2 Interchange migrations.** These are rearrangements in which two groups interchange their points of attachment. The name comprises: (a) the name of the migrating group of lower priority, preceded by the site designation 1/, (b) the name of the migrating group of higher priority, preceded by its initial site designation, and (c) the suffix "-interchange".

**Examples:**



Both transformations are examples of 1/*C*-hydro,5/*N*-chloro-interchange

**5.2.3 Other multiple migrations.** If more than one migration occurs within the transformation and the migrating groups do not simply exchange their positions, the transformation is named as a multi-migration, as in the following example:



**5.3 [x,y] Sigmatropic rearrangements** (where  $x, y \neq 1$ ). The names of these transformations take the form: (a-b)→(c-d)-*sigma*-migration, where a and b are the locants of the sites initially connected by the migrating sigma bond, and c and d are the locants of the sites to which it moves.

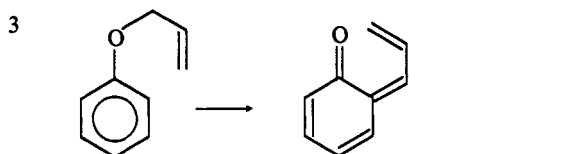
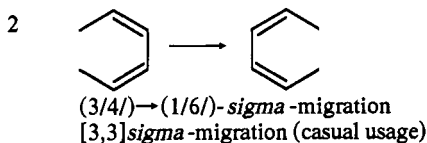
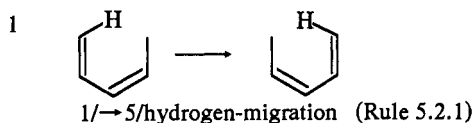
(Note 1: The use of the term "sigmatropic" in this rule has no mechanistic significance.)

(Note 2: Sigmatropic hydrogen shifts and other [1,x] rearrangements are named according to Rule 5.2.1.)

**5.3.1** In casual use in speech/writing the form [x,y]*sigma*-migration may be used, where x and y represent the number of atoms across which the ends of the migrating sigma bond move. (See Example 2.)

**5.3.2** In speech/writing atomic symbols may be omitted in the context of comparison with homoatomic substrates. (See Example 3.)

**Examples:**



Speech/writing:  $(3/O-4/)\rightarrow(1/6/)\text{-sigma-migration}$

or, for comparison with an all-carbon substrate:

$(3/4/)\rightarrow(1/6/)\text{-sigma-migration}$

or (casually) [3,3]*sigma*-migration

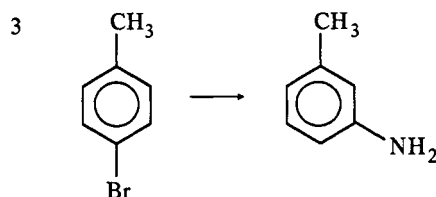
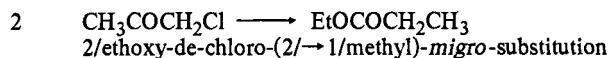
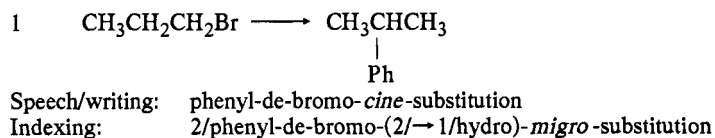
Indexing:  $(3/O-4/C)\rightarrow(1/C-6/C)\text{-sigma-migration}$

Note in Examples 2 and 3 that the locants are derived by numbering along a chain that is continuous in the substrate: Rule 0.3(a) is inapplicable, and the direction of numbering is determined from Rule 0.3(b,c).

**5.4 Migration accompanied by substitution.** The name is based on that for substitution without rearrangement, with the following modifications: (a) the site of the incoming group is designated relative to that of the leaving group, taken as 1/; (b) the italicised prefix "*migro*-" is inserted before "substitution"; (c) the migration is described by placing in parentheses immediately before "*migro*-": (i) the locants of the sites from which the migrating group departs and to which it moves, separated by an arrow ( $\rightarrow$ ), and (ii) the name of the migrating group.

**5.4.1** In speech/writing the term "*cine*" may be used in place of "(2/ $\rightarrow$ 1/hydro)-*migro*"; in such cases the initial locant 2/ may be omitted. This usage is common for aromatic substrates but need not be confined to them.

**Examples:**



Speech/writing: amino-de-bromo-*cine*-substitution  
Indexing: 2/amino-de-bromo-(2/ $\rightarrow$ 1/hydro)-*migro*-substitution



**5.5 Migration accompanied by addition, elimination, attachment, detachment, or other transformation.** The name is based on that of the transformation without rearrangement, with the following modifications: (a) the italicised prefix “*migro*-” is inserted before the characteristic suffix that defines the type of transformation; (b) the migration is described by placing in parentheses, immediately before “*migro*-”: (i) the site designations of the sites from which the migrating group departs and to which it moves, separated by an arrow ( $\rightarrow$ ), and (ii) the name of the migrating group.

**Examples:**

- 1  $\text{Ph-CO-CO-Ph} \longrightarrow \text{Ph}_2\text{C(OH)CO}_2^-$   
 Speech/writing: 1/*O*-hydro-3/oxido-(1/ $\rightarrow$ 2/phenyl)-*migro*-addition  
 Indexing: 1/*O*-hydro-3/*C*-oxido-(1/*C* $\rightarrow$ 2/*C*-phenyl)-*migro*-addition
- 2  $\text{Me}_3\text{C-CH}_2\text{Cl} \longrightarrow \text{Me}_2\text{C=CHMe}$   
 1/hydro,1/chloro-(2/ $\rightarrow$ 1/methyl)-*migro*-elimination
- 3  $\begin{array}{c} \text{Me}_2\text{C}-\text{CMe}_2 \\ | \quad | \\ \text{HO} \quad \text{OH} \end{array} \longrightarrow \text{Me}_3\text{C-CO-Me}$   
 Speech/writing: 1/*O*-hydro,3/hydroxy-(2/ $\rightarrow$ 3/methyl)-*migro*-elimination  
 Indexing: 1/*O*-hydro,3/*C*-hydroxy-(2/*C* $\rightarrow$ 3/*C*-methyl)-*migro*-elimination
- 4  $\text{Me-CO-CHN}_2 \longrightarrow \text{O=C=CHMe}$   
 dinitrogen-(2/ $\rightarrow$ 1/methyl)-*migro*-detachment
- 5  $(\text{PhCH}_2)_4\text{N}^+ \longrightarrow \text{PhCH}_2\text{CHPh-N}(\text{CH}_2\text{Ph})_2$   
 Speech/writing: hydron-(2/*N* $\rightarrow$ 1/benzyl)-*migro*-detachment  
 Indexing: hydron-(2/*N* $\rightarrow$ 1/*C*-benzyl)-*migro*-detachment

## 6 COUPLING AND UNCOUPLING TRANSFORMATIONS

### 6.1 Scope of the Rule

This rule is designed to cover transformations such as  $2 \text{ A-B} \longrightarrow \text{A}_2$ . This could formally be named according to Rule 2 as a substitution, “A-de-B-substitution”, but such a name disguises the symmetry of the transformation. To emphasise this, the “coupling” nomenclature is used. Likewise,  $\text{A}_2 \longrightarrow 2 \text{ A}$  could be named by Rule 4.2 “A-detachment”, but again the symmetry can be described better by using a special “uncoupling” nomenclature. (Compare also the discussion of “aggregating” substitutions, Rule 1.3.)


Note that this rule is applicable only to truly symmetrical transformations. For example  $2 \text{ Ph-Br} \longrightarrow \text{Ph}_2$  is a coupling.  $2 \text{ Ph-N}_2^+ \longrightarrow \text{Ph-N=N-Ph}$  is not, because the nitrogen atoms of the product do not derive symmetrically from the substrate. Such a transformation should be represented as  $\text{Ph-N}_2^+ \longrightarrow \text{Ph-N=N-Ph}$  (since only one of the diazonium entities is a substrate) and named according to Rules 1 or 2 as “*N*-benzenide-attachment” or “phenylazo-de-diazonio-substitution”. A transformation may be regarded as symmetrical at different levels of generality. Thus  $\text{Ph-Cl} + \text{Ph-Br} \longrightarrow \text{Ph}_2$ , a reaction in which the different halogens are specified, cannot be described as a symmetrical transformation; however,  $2 \text{ Ph-Hal} \longrightarrow \text{Ph}_2$  is symmetrical at the generic level. Likewise  $\text{C}_6\text{H}_5\text{Br} + \text{CH}_3\text{C}_6\text{H}_4\text{Br} \longrightarrow \text{C}_6\text{H}_5\text{-C}_6\text{H}_4\text{-CH}_3$  is not a coupling transformation, though it belongs to the general class of couplings represented by  $2\text{ArBr} \longrightarrow \text{Ar}_2$ . For a transformation to be treated as a coupling, the substrate must appear with the stoichiometric coefficient of 2, the product must be symmetrical about a newly formed bond, and the two half-product moieties must be of equal provenance. To be treated as an uncoupling the substrate must be symmetrical about a bond that is cleaved, and the product must appear with the stoichiometric coefficient of 2.

In most of these transformations the symmetry requires that an attaching or detaching entity be given a name appropriate to a particular oxidation level (see Table 1). Thus in Example 1 of Rule 6.2.1 the transformation of  $2\text{PhBr}$  into  $\text{Ph}_2$ , regardless of the mechanism of the actual reaction, must be described in terms of the detachment of a bromine atom from each substrate molecule and the coupling of the resulting phenyl radicals. However, when more than one group is detached (Example 8, Rule 6.2.1) or attached (Example, Rule 6.3.2), or when groups are both attached and detached (Example 1, Rule 6.4), there is no implied oxidation level and group names (Table 1) are appropriate.

**6.2 Coupling transformations with detachment.** These are transformations in which one or more univalent or multivalent groups or entities are detached identically from each of the two substrate entities and the remaining fragments of the substrate become coupled.

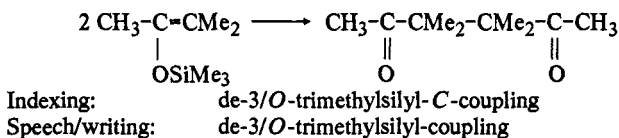
6.2.1 If the coupling occurs at the same site from which the leaving groups or entities detach, then the name comprises: (a) the syllable “de-”, (b) the name(s) of the detached fragment or fragments, and (c) the suffix “-coupling”.

**Examples:**

- 1  $2 \text{ C}_6\text{H}_5\text{Br} \longrightarrow \text{C}_6\text{H}_5\text{-C}_6\text{H}_5$   
de-bromine-coupling
  - 2  $2 \text{ C}_6\text{H}_5\text{COCH}_3 \longrightarrow \text{C}_6\text{H}_5\text{COCH}_2\text{-CH}_2\text{CO C}_6\text{H}_5$   
de-hydrogen-coupling
  - 3  $2 \text{ CH}_3\text{CH}_2\text{SH} \longrightarrow \text{CH}_3\text{CH}_2\text{S-S CH}_2\text{CH}_3$   
S-de-hydrogen-coupling
  - 4  $2 \text{ Pr}_2\text{C=NNH}_2 \longrightarrow \text{Pr}_2\text{C=N-N-CPr}_2$   
N-de-aminyl-coupling
  - 5  $2 \text{ CH}_3\text{CH}_2\text{CH=O} \longrightarrow \text{CH}_3\text{CH}_2\text{CH=CHCH}_2\text{CH}_3$   
de-oxygen-coupling
  - 6  $2 \text{ Ph}_2\text{C=N}_2 \longrightarrow \text{Ph}_2\text{C=CPh}_2$   
de-dinitrogen-coupling
  - 7   
de-sulfur-coupling
  - 8  $2 (\text{C}_6\text{H}_5)_2\text{CHCl} \longrightarrow (\text{C}_6\text{H}_5)_2\text{C=C}(\text{C}_6\text{H}_5)_2$   
de-hydro,chloro-coupling
  - 9  $2 \text{ C}_6\text{H}_5 \text{NO}_2 \longrightarrow \text{C}_6\text{H}_5 \text{N=N C}_6\text{H}_5$   
N-de-bisoxxygen-coupling
- Note that “bisoxxygen” is used to describe two separate oxygen atoms, as opposed to “dioxygen” which indicates molecular O<sub>2</sub>.
- 10  $2 \text{ C}_6\text{H}_5\text{CO-OO-C}(\text{CH}_3)_3 \longrightarrow \text{C}_6\text{H}_5\text{-C}_6\text{H}_5$   
de-[*tert*-butylperoxy-carbonyl]-coupling
  - 11  $2 (\text{CO})_5\text{W=C}(\text{C}_6\text{H}_5)_2 \longrightarrow (\text{C}_6\text{H}_5)_2\text{C=C}(\text{C}_6\text{H}_5)_2$   
de-[pentacarbonyltungsten]-coupling

6.2.2 If the site of coupling differs from that from which any of the groups or entities detach, then appropriate site designations are placed before the names of the detaching groups or entities, the site of coupling being implicitly 1/ (an exception to Rule 0.3.). If any of the reacting sites is other than carbon, then appropriate atomic symbols are used according to Rule 0.3.1, the symbol for the site of coupling being placed before the suffix “-coupling”.

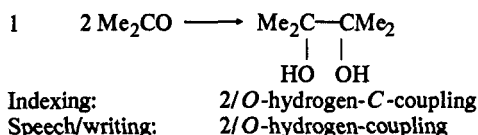
**Example:**

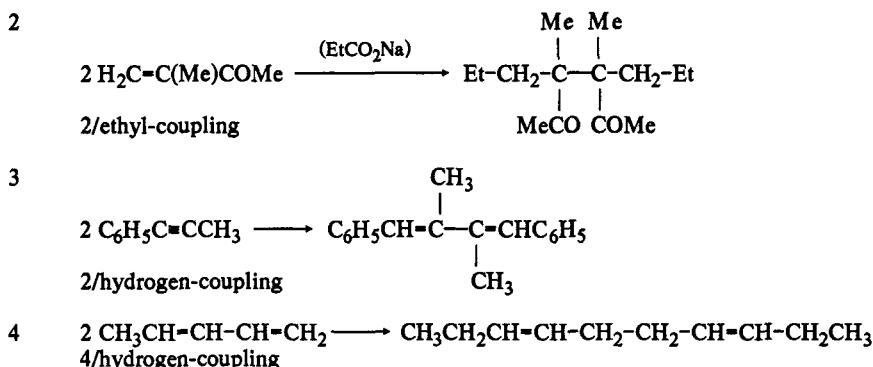


6.3 **Coupling transformations with attachment.** These are transformations in which one or more univalent or multivalent groups or entities are attached identically to two unsaturated substrate entities, and the resulting fragments become coupled at a site that was part of the unsaturated system.

6.3.1 If the attachment occurs at a single site the name comprises: (a) the names of any attaching groups or entities preceded by the appropriate site designation relative to the site of coupling which (in an exception to Rule 0.3) is taken implicitly to be 1/, and (b) the suffix “-coupling”. Rule 6.2.2 also applies to these transformations.

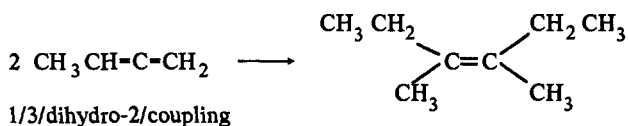
**Examples:**





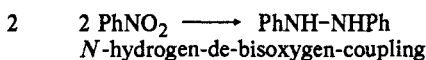
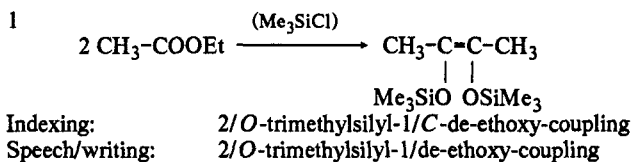
6.3.2 If attachments occur at more than one site then Rule 6.3.1 is applied with the modification that, if the site of coupling is between the extreme sites of attachment, then the designation 1/ is given to one of the sites of attachment (chosen according to Rule 0.3), and the appropriate site designation is placed before the term "coupling".

**Example:**



6.4 **Coupling transformations with attachment and detachment.** These transformations are named by combining appropriate terms as laid down in Rules 6.2 and 6.3, with the attaching groups named before the detaching groups. Unless all the attachments and detachments occur at the site of coupling, the site designation 1/ should not be omitted. (See example 1.)

**Examples:**

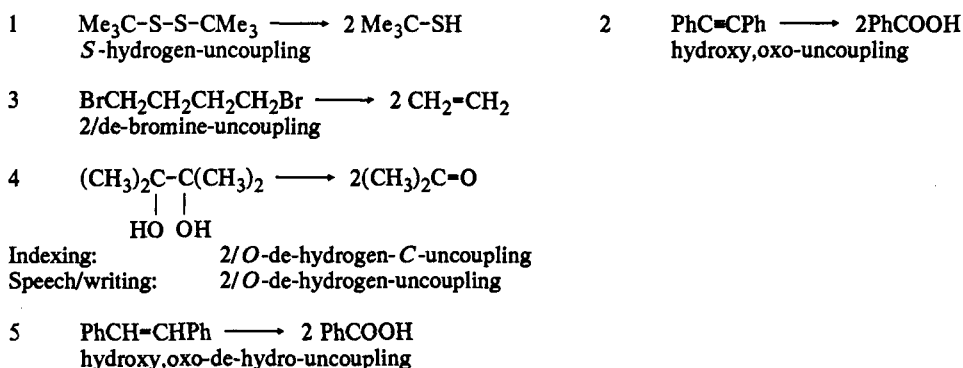


Note: In this rather unusual example one cannot avoid indicating oxidation levels for the attaching and detaching entities, even though there is no intention of implying a mechanism. The term "bisoxygen" is used to describe two separate oxygen atoms, as opposed to "dioxigen" which refers to molecular  $\text{O}_2$ .

6.5 **Uncoupling transformations.** These are transformations in which a symmetrical substrate is cleaved into two identical fragments which may then undergo attachment, detachment or both.

The name comprises: (a) the names of any attaching groups or entities, (b) the names of any detaching groups or entities preceded by the syllable "de-", and (c) the term "-uncoupling". Site designations are used as in naming coupling transformations (Rules 6.2 - 6.4.)

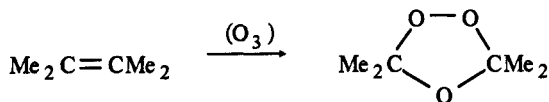
**Examples:**





**7.1.2 Biinsertions** are named in the same way as the monoinsertions of Rule 7.1.1 except that: (a) the initial italicised atomic symbols are enclosed in parentheses and followed by a subscript "2"; (b) if the two entities that are inserted are the same their name is preceded by "bis", otherwise their names are separated by commas (or, if the names are complex, they are placed in separate pairs of square brackets) and listed in order of (i) increasing length of the chain between sites of attachment or, if that is insufficient to decide, (ii) decreasing atomic number of the elements at the site(s) of attachment at the first point of difference; and (c) the suffix is "-biinsertion".

**Example:**



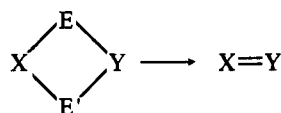
oxy,peroxy-biinsertion

**7.2 Extrusion transformations.** Extrusion transformations are those transformations in which a divalent group (-E-) that was covalently bonded to two other atoms, is expelled with the result that connectivity between these two atoms is established:

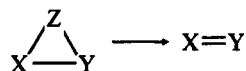


Since the naming of transformations is independent of the reaction mechanism, extrusions can also be considered to be substitutions. When it is known that one of the groups X or Y departs from the substrate and is replaced in the product by an identical group from the reactants or from the solvent (as shown by isotopic labelling, for example), the name obtained by considering the transformation as a substitution is usually preferred.

Usually the word "extrusion" refers to transformations which result in the formation of a single bond between X and Y. These rules are extended to *biextrusions* which are of the type:



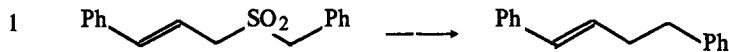
Transformations of the type:



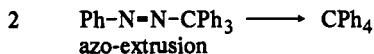
in which there is no change of connectivity between X and Y are excluded. They are named according to the Rules for ring-opening (8.5).

**7.2.1** The name for a **monoextrusion** transformation comprises: (a) the italicized atomic symbols of the two atoms that become bonded together in order of decreasing atomic weight (if both atoms are carbon, the symbols are omitted); (b) the name of the divalent group that is extruded from the substrate; and (c) the suffix "-extrusion".

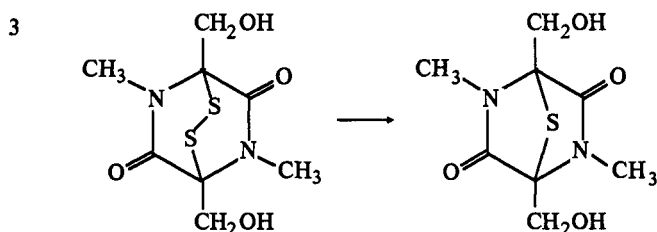
**Examples:**



sulfonyl-extrusion



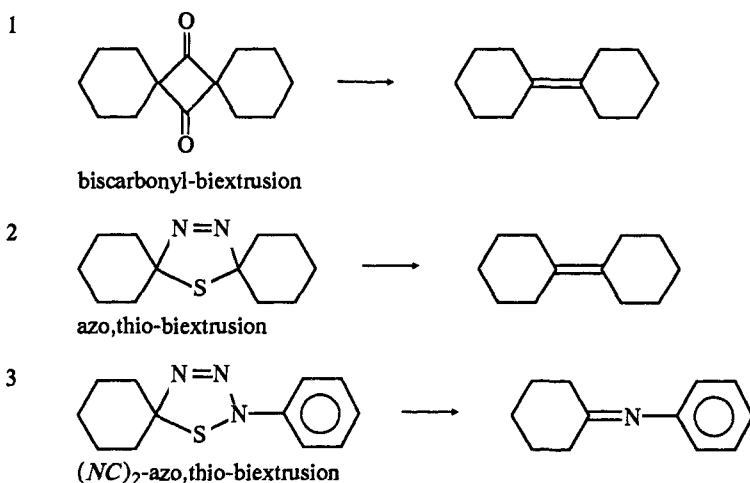
azo-extrusion



SC-thio-extrusion

**7.2.2 Biextrusions** are named in the same way as the monoextrusions of Rule 7.2.1 except that: (a) the initial italicised atomic symbols are enclosed in parentheses and followed by a subscript "2"; (b) the two entities that are extruded are treated as in Rule 7.1.2; and (c) the suffix is "-biextrusion".

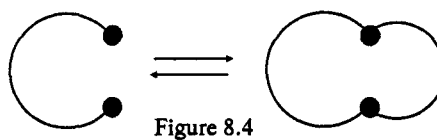
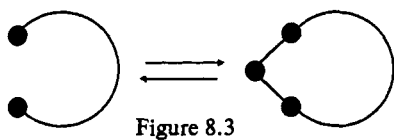
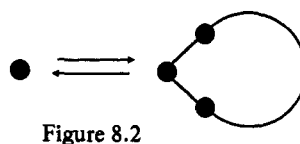
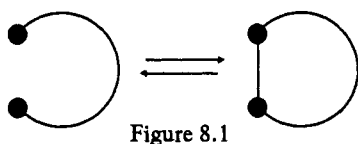
**Examples:**



## 8 RING CLOSING AND RING OPENING TRANSFORMATIONS

The ring closing transformations described under this Rule are those in which a single ring is formed either by the intramolecular cyclisation of an open chain (Figure 8.1) or by the making of two bonds between a single atom of the substrate and different atoms of a reagent (Figure 8.2), or between different atoms of the substrate and a single atom of a reagent (Figure 8.3), or between different atoms of the substrate and of a reagent (Figure 8.4). The ring openings are the reverse of these transformations.

Transformations in which the size of an already existing ring is altered are named according to the rules for acyclic transformations. Some also appear in the list of complex transformations (Section 9).



### 8.1 General information

**8.1.1** The names for all ring closing and ring opening transformations are based on those of related acyclic transformations prefixed by "*cyclo*" for ring closings or "*seco*" for ring openings. In intramolecular transformations (Figure 8.1) the same entity is both substrate and reagent, and according to the principle enunciated in the Preamble whereby the name is independent of the nature of the substrate, it is necessary to confine the names of such transformations to generic forms.

**8.1.2** If, in a ring closure that entails an addition transformation to a multiple bond, the site of addition that does not receive the ring-closing bond is incorporated into the new ring, then in speech/writing the prefix "*endo*" may optionally be inserted before the name; if it is not so, the prefix "*exo*" may be used. The prefixes may similarly be used in ring-opening eliminations.

**8.1.3** The italicised atomic symbols of the elements at each end of the new bond(s) (in ring closings) or of the breaking bond(s) (in ring openings) are placed at the start of the name, being listed in order of decreasing atomic weight. For intermolecular transformations (Figures 8.2 – 8.4) the two pairs of symbols are separated by a comma. When all the atoms involved are carbon the symbols are omitted. When the context makes the nature of the transformation clear, it may be permissible to omit other symbols, especially in casual use in speech (see Examples 1, 8 and 9 of Rule 8.4.1; Example 2 of Rule 8.4.2; Example 2 of Rule 8.5.1; Example 1 of Rule 8.5.2).

**8.1.4 Ring size.** In speech/writing names the size of the ring formed or opened may optionally be shown in parentheses before the name. For intramolecular transformations (Figure 8.1) the ring size is given as a single number. In transformations in which two rings open to form a single larger ring, or in the reverse ring closings, one ring size or both, separated by a comma and starting with the smaller, may be included. For intermolecular transformations two numbers are used in the form (m+n), where m is the number of atoms in the ring deriving from the reagent (in ring closings) or lost from the substrate (in ring openings) and n is the number deriving from the substrate (in ring closings) or retained in the product (in ring openings): compare examples under Rules 8.4. and 8.5. In naming classes of transformations in which a range of ring sizes may be involved (for example, a series of *cycloalkoxy*-dehydroxylations of hydroxyacids, "lactonizations") the letters n and/or m may be used in place of numbers.

**8.1.5** In electrocyclic ring openings and closings and in cycloadditions and cycloeliminations the formal rearrangement of  $\pi$ -bonds that accompanies the transformation is not a part of the name but may be indicated in a parenthetical phrase (Example 2 under Rule 8.2.1).

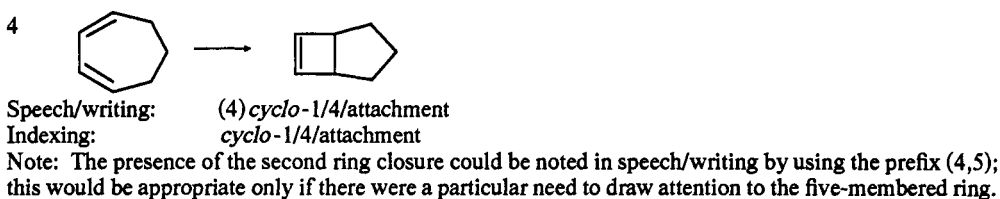
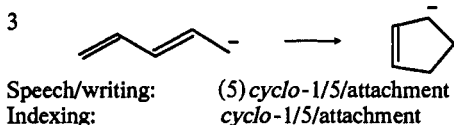
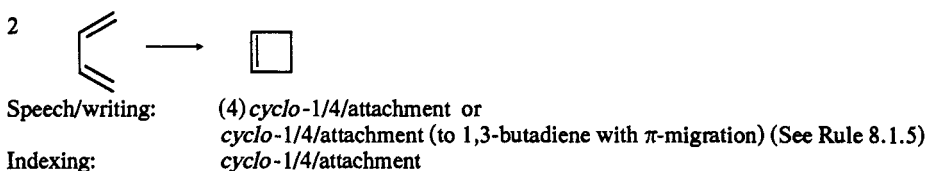
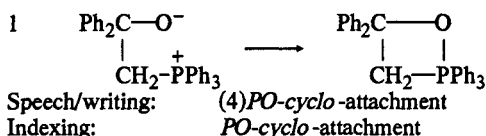
## 8.2 Intramolecular cyclisation transformations (Figure 8.1)

### 8.2.1 Ring formation involving intramolecular attachment

The name for these transformations comprises (a) the appropriate prefixes according to Rule 8.1, and (b) the term "-*cyclo-attachment*".

When the attachment involves the formation of a single bond across a system of conjugated multiple bonds (electrocyclic ring formation) the relative positions of the sites between which the new bond is formed are inserted after "*cyclo*".

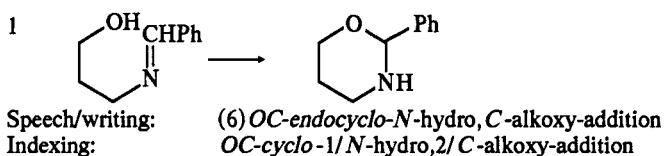
#### Examples:

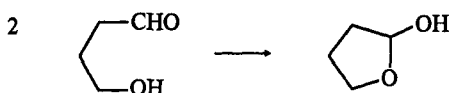


**8.2.2 Ring formation via intramolecular addition, insertion or substitution transformations.** If the transformation entails addition to a multiple bond or to a carbene, nitrene or similar electron-deficient species, then it is named as an addition regardless of what other transformations may be involved (Example 3). If it can be named as an insertion into a single bond but not as an addition, then it is named as an insertion (Example 7). Otherwise it is named as a substitution. If it could be named as either of two substitutions, that in which the leaving group has higher priority (Rule 0.2) should normally be preferred (Example 9).

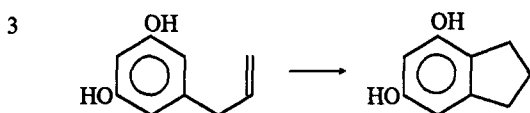
The name is then formed as follows. (a) The two ring-closing sites are treated as if they were not connected to each other by a common chain and are named generically. The name for the transformation is then determined according to the rules for acyclic transformations. (b) The name so formed is prefixed according to Rule 8.1.

#### Examples:

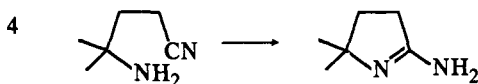




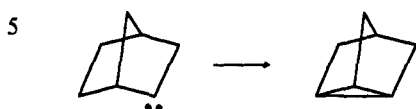
Speech/writing: (5) *OC-exocyclo-O-hydro, C-alkoxy-addition*  
 Indexing: *OC-cyclo-1/O-hydro, 2/C-alkoxy-addition*



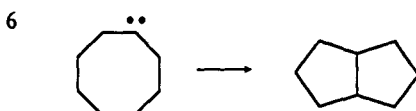
Speech/writing: (5) *endocyclo-hydro, aryl-addition*  
 Indexing: *cyclo-hydro, aryl-addition*  
 Note: not named as an aromatic substitution.



Speech/writing: (5) *NC-exocyclo-1/1/N-dihydro-2/alkylimino-biaddition*  
 Indexing: *NC-cyclo-1/1/N-dihydro, 2/C-alkylimino-biaddition*

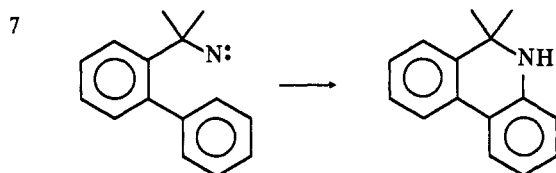


Speech/writing: (3) *cyclo-CH-[alkane-1/1/diyl]-insertion*  
 Indexing: *cyclo-CH-[alkane-1/1/diyl]-insertion*



*cyclo-CH-[alkane-1/1/diyl]-insertion*

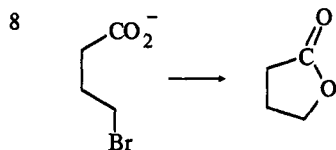
In speech/writing this name could be prefixed by (5) or by (5,5) if desired.



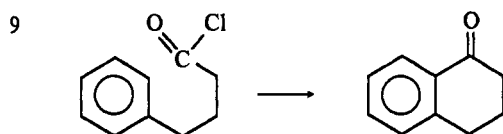
*NC-cyclo-CH-imino-insertion*

In speech/writing the prefix (6) may be used.

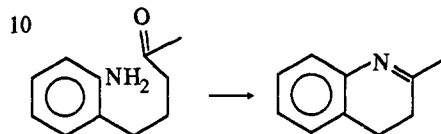
Note: not named as an aromatic substitution.



Speech/writing: (5) *OC-cyclo-acyloxy-de-bromination*  
 Indexing: *OC-cyclo-acyloxy-de-bromo-substitution*



Speech/writing: (6) *cyclo-aryl-de-chlorination*  
 preferred to *cyclo-acyl-de-hydrogenation*  
 Indexing: *cyclo-aryl-de-chloro-substitution*



*NC-cyclo-arylimino-de-oxo-bisubstitution*  
 In speech/writing the prefix (6) may be used.

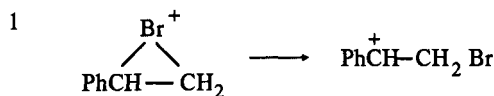


**8.3 Non-fragmenting ring opening transformations.** (Ring openings in which the ring is broken at only one point, so that the atoms that constituted the ring remain in a continuous chain. Compare Figure 8.1.)

**8.3.1 Ring opening involving intramolecular detachment.** The name for these transformations comprises: (a) the appropriate prefixes according to Rule 8.1, and (b) the term “-*seco*-detachment”.

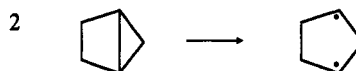
When the detachment involves the cleavage of a single bond and the formation of a system of conjugated multiple bonds (electrocyclic ring opening) the relative positions of the sites between which the breaking bond is located, numbered through the conjugated system, are inserted after “*seco*”.

**Examples:**



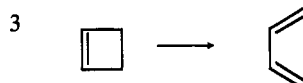
*BrC-seco*-detachment

In speech/writing the prefix (3) may be used.



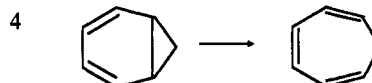
*seco*-detachment

In speech/writing the prefix (3,4) may be used.



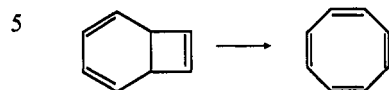
*seco*-1/4/detachment

In speech/writing the prefix (4) may be used.



*seco*-1/6/detachment

In speech/writing the prefix (3,6) may be used.



This transformation could be named (in speech/writing) as either

(4,6)*seco*-1/4/detachment or (4,6)*seco*-1/6/detachment.

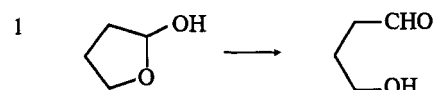
The prefix (4,6) is optional in speech/writing, and in the indexing name it is omitted.

**8.3.2 Ring cleavage via intramolecular elimination, extrusion or substitution transformations.**

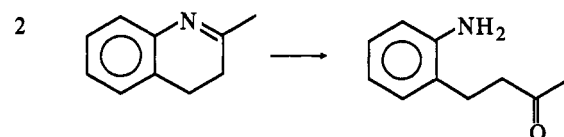
If the transformation entails elimination to form a multiple bond or a carbene, nitrene or similar electron-deficient species, then it is named as an elimination regardless of what other transformations may be involved. If it can be named as an extrusion but not as an elimination, then it is named as an extrusion. Otherwise it is named as a substitution. If it could be named as either of two substitutions, that in which the entering group has higher priority (as defined in Rule 0.2) should normally be preferred.

The name is then determined according to the rules for acyclic transformations and the fact that the transformation entails a ring opening is indicated by prefixes according to Rule 8.1.

**Examples:**



Speech/writing: (5)*OC-exoseco*-*O*-hydro,*C*-alkoxy-elimination  
Indexing: *OC-seco*-1/*O*-hydro,2/*C*-alkoxy-elimination



*NC-seco*-oxo-de-arylimino-bisubstitution  
preferred to: *NC-seco*-dihydro-de-alkylidene-bisubstitution  
For speech/writing the prefix (6) may be used.

**8.4 Intermolecular cyclisation transformations** (Figures 8.2 – 8.4)

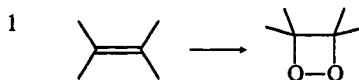
**8.4.1 Cycloaddition transformations** (in which a ring is formed by the transformation of  $\pi$ -bonds of the substrate into new  $\sigma$ -bonds to a divalent group derived from the reagent). In the names of these transformations no distinction is made between concerted and non-concerted processes.

The name of these transformations comprises: (a) the appropriate prefixes according to Rule 8.1; (b) the name of the group that is added to the substrate; (c) the relative positions of the substrate to which addition occurs; and (d) the suffix “-addition”.

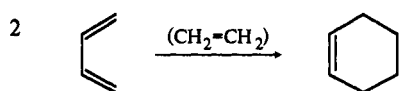
In (1+2) cycloadditions, that is, when new bonds are formed from adjacent substrate atoms to the same addend atom to form a three-membered ring, the prefix “*epi*” may be used in speech/writing in place of “(1+2)*cyclo*”.

Note that in these Rules the use of parentheses to enclose ring-size numbers is in deliberate contrast to the customary use of square brackets in describing, for example, the Diels-Alder reaction as a [2+4]cycloaddition. This is to emphasise that the name of a transformation has no mechanistic implication.

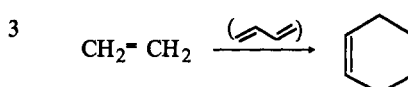
**Examples:**



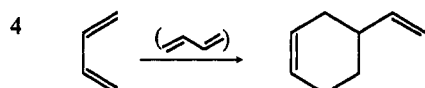
Speech/writing: (2+2)*OC,OC-cyclo*-peroxy-1/2/addition  
In casual usage this could be abbreviated to: *cyclo*-peroxy-addition.  
Indexing: *OC,OC-cyclo*-peroxy-1/2/addition



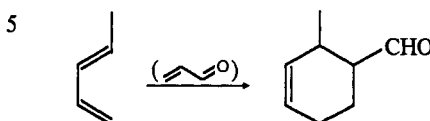
*cyclo*-ethylene-1/4/addition  
In speech/writing the prefix (2+4) may be used.



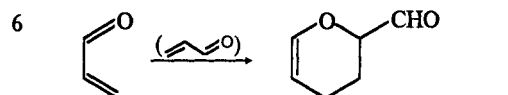
*cyclo*-[but-2-ene-1,4-diyl]-1/2/addition  
In speech/writing the prefix (4+2) may be used.



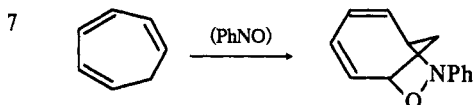
*cyclo*-[but-1-ene-3,4-diyl]-1/4/addition  
In speech/writing the prefix (2+4) may be used.



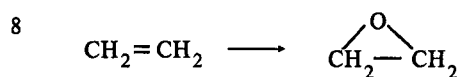
*cyclo*-[formylethylene]-1/4/addition  
In speech/writing the prefix (2+4) may be used.  
Note: examples 2,4 and 5 are all generically:  
*cyclo*-[alkane-1/2/diyl]-1/4/addition



*OC,CC-cyclo*-[formylethylene]-1/4/addition  
In speech/writing the prefix (2+4) may be used.



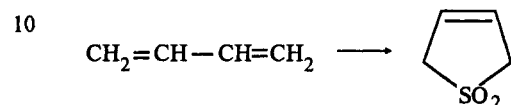
*OC,NC-cyclo*-[phenyliminoxy]-1/6/addition  
In speech/writing the prefix (2+6) may be used.



Speech/writing: *epi*-oxy-addition  
Indexing: *OC,OC-cyclo*-oxy-1/2/addition



Speech/writing: *epi*-bromoniumdiyl-addition or  
(1+2)*BrC,BrC-cyclo*-bromoniumdiyl-1/2/addition  
Indexing: *BrC,BrC-cyclo*-bromoniumdiyl-1/2/addition

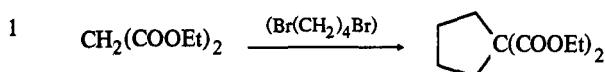


*SC,SC-cyclo*-sulfonyl-1/4/addition  
In speech/writing the prefix (1+4) may be used.

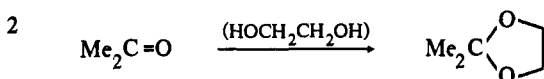
**8.4.2 Transformations in which the ring is closed by a multivalent substitution at a single atom of substrate or reagent** (Figures 8.2 and 8.3). If the single atom entity is the substrate (Figure 8.2) the transformation is named according to Rule 1.2 for acyclic multivalent substitutions, with appropriate prefixes according to Rule 8.1. (Examples 1 and 2.)

If the single atom fragment comes from the reagent (Figure 8.3), the transformation is named similarly but without the multiplicity prefixes (bi, ter, etc.) and with the addition of relative positional numbers before the suffix "substitution". (Examples 3 and 4.)

**Examples:**



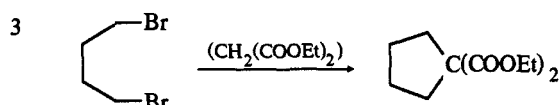
*cyclo*-tetramethylene-de-dihydro-bisubstitution  
In speech/writing the prefix (4+1) may be used



Speech/writing: (4+1)*OC, OC-cyclo*-ethylenebisoxo-de-oxo-bisubstitution

Or in casual usage: *cyclo*-ethylenebisoxo-de-oxo-bisubstitution

Indexing: *OC, OC-cyclo*-ethylenebisoxo-de-oxo-bisubstitution

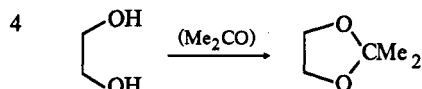


Indexing:

specific: *cyclo*-[di(ethoxycarbonyl)methylene]-de-dibromo-1/4/substitution

generic: *cyclo*-alkane-1/1/diyl-de-dihalo-1/4/substitution

In speech/writing the prefix (1+4) may be used.



*OC, OC-cyclo*-[propane-2,2-diyl]-de-dihydro-1/O,4/O-substitution

In speech/writing the prefix (1+4) may be used.

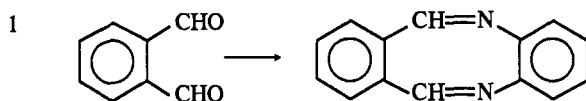
By contrast with example 2, it would not be desirable to omit all atomic symbols, even in casual usage, from this name because there is no other way of showing the involvement of oxygen atoms in the ring closing process.

**8.4.3 Ring closing transformations involving the formation of bonds at two independent sites** (Figure 8.4). The two bond-making transformations are named as for the corresponding acyclic transformations. The names used for groups entering into one bond-making transformation are chosen as though the other bond had not yet closed.

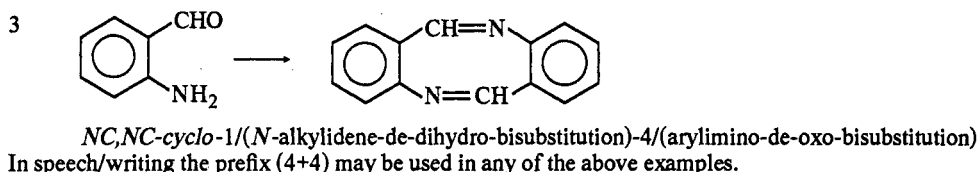
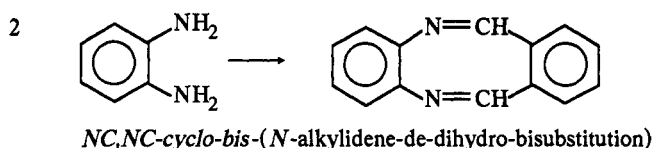
If the two bond-making transformations are the same, the complete transformation is named by placing the name of the acyclic transformation in parentheses and prefixing it with "*cyclo-bis*-" and with other appropriate prefixes according to Rule 8.1.

If the two bond-making transformations differ, the resulting names are usually too complicated for convenient use (see Section 4 of the Preamble). However, if a name is required it is constructed as follows. The names of the two single transformations are separately enclosed in parentheses, prefixed by relative positional numbers of the ring closing sites, joined by a hyphen, and the whole is prefixed according to Rule 8.1. Substitutions are named before additions or eliminations. (Compare the Example under Rule 8.5.3). If the two transformations are of the same type they are named in such an order that at the first point of difference a group of lower valency or of lower priority according to Rule 0.2 appears in the first name.

**Examples:**



*NC, NC-cyclo-bis*-(arylimino-de-oxo-bisubstitution)



## 8.5 Fragmenting ring opening transformations (Figs. 8.2 - 8.4)

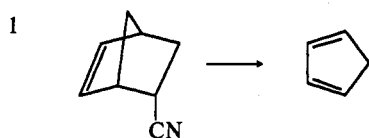
**8.5.1 Cycloelimination transformations** (in which a ring is broken by the transformation of  $\sigma$ -bonds of the substrate into new  $\pi$ -bonds in the product). In the names of these transformations no distinction is made between concerted and non-concerted processes.

The name of these transformations comprises: (a) the appropriate prefixes according to Rule 8.1; (b) the name of the divalent group that is eliminated from the substrate; (c) the relative positions of the product from which elimination occurred; and (d) the suffix "-elimination".

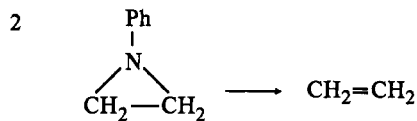
In (1+2)cycloeliminations, that is, when a three-membered ring is opened with a single ring atom departing in the eliminand, the prefix "*epi*" may be used in speech/writing in place of "(1+2)*seco*".

Note that in these Rules the use of parentheses to enclose ring-size numbers is in deliberate contrast to the customary use of square brackets in describing, for example, the retro-Diels-Alder reaction as a [2+4] cycloelimination. This is to emphasise that the name of a transformation has no mechanistic implication.

### Examples:



*seco*-[cyanoethylene]-1/4/elimination  
In speech/writing the prefix (2+4) may be used.

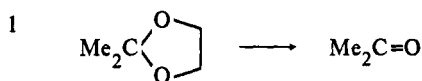


*NC,NC-seco*-phenylimino-1/2/elimination  
In speech/writing a generic name for this transformation could be: *epi*-imino-elimination

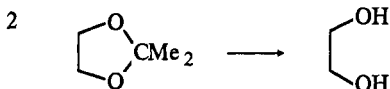
**8.5.2 Transformations in which the ring is opened by a multivalent substitution at a single atom or with a single atom of the ring as the leaving group in two ring-opening substitutions** (Figures 8.2 and 8.3). If the single atom entity is the site of substitution (Figure 8.2) the transformation is named according to Rule 1.2 for acyclic multivalent substitutions, with appropriate prefixes according to Rule 8.1.

If the single atom fragment departs as the leaving group (Figure 8.3), the transformation is named similarly but without the multiplicity prefixes (bi, ter, etc.) and with the addition of relative positional numbers before the suffix "substitution".

### Examples:



*OC,OC-seco*-oxo-de-ethylenebisoxo-bisubstitution  
In speech/writing the prefix (1+4) may be used.  
In casual usage the name could be abbreviated to:  
*seco*-oxo-de-ethylenebisoxo-bisubstitution



*OC,OC-seco*-dihydro-de-[propane-2,2-diy]-1/*O*,4/*O*-substitution  
In speech/writing the prefix (4+1) may be used.

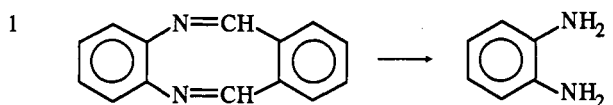
By contrast with example 1, it would not be desirable to omit all atomic symbols, even in casual usage, from this name: there is no other way of showing the involvement of oxygen atoms in the ring opening process.

**8.5.3 Ring opening transformations involving bond breaking at two independent sites** (Figure 8.4). The two bond-breaking transformations are named as for the corresponding acyclic transformations. The names used for groups entering into one bond-breaking transformation are chosen as though the other bond had not already opened.

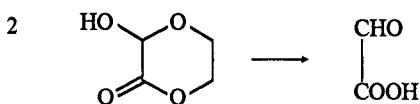
If the two bond-making transformations are the same, the complete transformation is named by placing the name of the acyclic transformation in parentheses and prefixing it with “*seco-bis-*” and with other appropriate prefixes according to Rule 8.1.

If the two bond-making transformations differ, the resulting names are usually too complicated for convenient use (see Section 4 of the Preamble). However, if a name is required it is constructed as follows. The names of the two single transformations are separately enclosed in parentheses, prefixed by relative positional numbers of the ring opening sites, joined by a hyphen, and the whole is prefixed according to Rule 8.1. Substitutions are named before additions or eliminations. If the two transformations are of the same type they are named in such an order that at the first point of difference a group of lower valency or of lower priority according to Rule 0.2 appears in the first name.

**Examples:**



*NC,NC-seco-bis-*(dihydro-de-alkylidene-bisubstitution)



*OC,OC-seco-1/(hydroxy-de-alkoxy-substitution)-2/(1/O-hydro-2/C-alkoxy-elimination)*

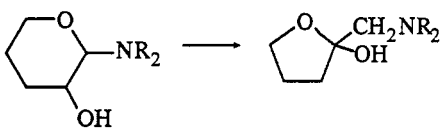
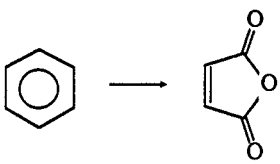
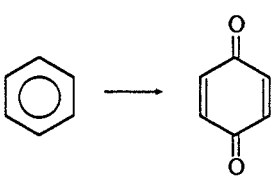
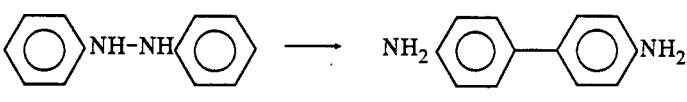
## 9 COMPLEX TRANSFORMATIONS


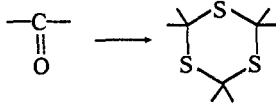
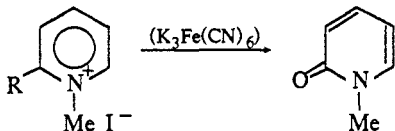
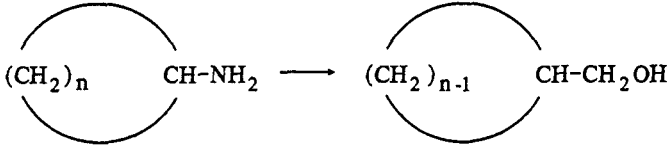
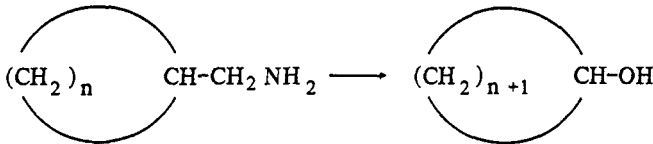
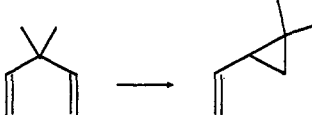
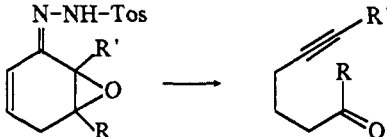
In this section will be found a list of transformations in which the bond changes are too complex to be dealt with by simple systematic nomenclature. Each of the transformations is individually named.

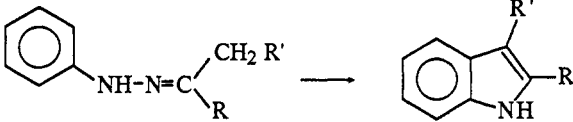
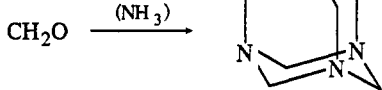
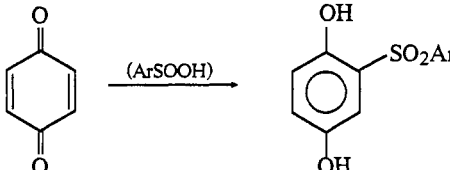
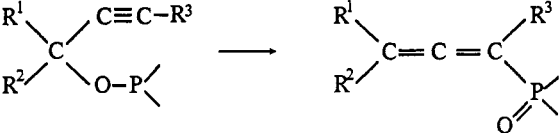
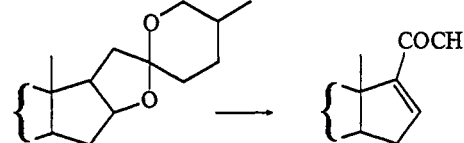
The list of complex transformations given here is not exhaustive, nor could it be. The literature contains far too many complex transformations that are mentioned only once or a few times. In this list the Commission has endeavoured to give those that are relatively common. It is intended that the list will be modified from time to time to add names as new transformations are discovered, and to delete names as the systematic rules are extended. For example, the transformation listed below as the carbonyl-trithiane transformation is a relatively simple “aggregating” substitution, but the present rules cannot cover this and ring closing simultaneously.

In most cases the names given for the transformations listed here are modified forms of those in common use. Where a transformation lacked such a name, a new name has been devised. In some cases, a single name is used for a family of closely related transformations. These cases are grouped at the end of the list. Organic chemistry has long had a large number of “name reactions”, and some of these are on our list, e.g., Beckmann rearrangement, Fischer indole synthesis, acyloin condensation. In most cases a word or two has been added to provide a bit more information. Thus, the Beckmann rearrangement is here called the Beckmann oxime-amide rearrangement, but many of these names will still be familiar to most organic chemists. Not all of the “name reactions” of organic chemistry are on our list. Many can be named by the systematic rules given earlier in this document, and, where possible, should be named in that way. Thus the Rosenmund reduction would now be hydro-de-chlorination or hydro-de-chloro-substitution. However, there may be times when the older names are preferable. “Hydro-de-chlorination” refers to a *transformation*, “Rosenmund reduction” to a particular *reaction* procedure. The processes  $\text{CH}_3\text{Cl} \rightarrow \text{CH}_4$  and even  $\text{CH}_3\text{COCl} (+ \text{LiAlH}(\text{O}-t\text{-Bu})_3) \rightarrow \text{CH}_3\text{CHO}$  are also hydro-de-chlorination, but they are not the Rosenmund reduction, in which acyl halides are reduced to aldehydes by hydrogenation with certain catalysts. Consequently, even though the systematic names for transformations will prove very useful, they are not likely to completely supersede all of the older names; nor does the Commission so recommend. For convenience, a list of some of the “name reactions” that can be named as systematic transformations is given in the Appendix at the end of these rules. Note that several of these can be named in two ways, depending on the substrate.

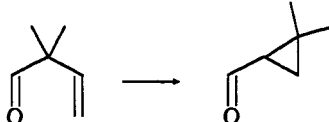
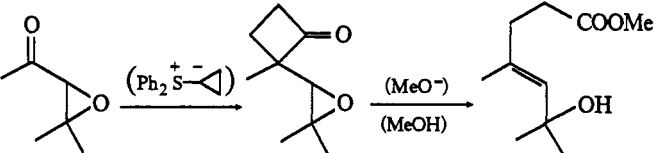
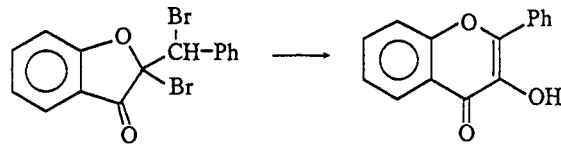
## List of Complex Transformations

Name	Transformation
Acyloin ester condensation	$2 \text{RCOOR}' \longrightarrow \text{RCH(OH)COR}$
Aldehyde-oxirane transformation	$2 \text{RCHO} \longrightarrow \text{RCH} \begin{array}{c} \text{---} \text{CHR} \\ \diagdown \quad \diagup \\ \text{O} \end{array}$
Alkene-halooxime transformation	$>\text{C}=\text{CH}- \longrightarrow >\text{CCl}-\text{C}(=\text{NOH})-$
Alkenyl azide-azirene transformation	$>\text{C}=\text{CR}-\text{N}_3 \longrightarrow >\text{C} \begin{array}{c} \text{N} \\ \diagdown \quad \diagup \\ \text{---} \text{CR} \end{array}$
Amadori rearrangement	 <p>This can also be represented:</p> $\begin{array}{c} \text{CH}=\text{NR}_2 \\   \\ \text{CH}-\text{OH} \\   \end{array} \longrightarrow \begin{array}{c} \text{CH}_2\text{NR}_2 \\   \\ \text{C}=\text{O} \\   \end{array}$
Arene-anhydride oxidation	
Arene-quinone transformation	
Baeyer-Chichibabin pyridine synthesis	$4 \text{CH}_3\text{CHO} \xrightarrow{(\text{NH}_3)} \text{Me} \begin{array}{c} \diagup \quad \diagdown \\ \text{---} \text{N} \end{array} \text{Et} \text{ or } \begin{array}{c} \text{Me} \\   \\ \text{---} \text{N} \\   \\ \text{Et} \end{array}$
Beckmann oxime-amide rearrangement	$\text{R}-\text{C}-\text{R}' \xrightarrow{\text{NOH}} \text{R}-\text{NH}-\text{CO}-\text{R}'$
Benzidine rearrangement	
Benzoin aldehyde condensation	$2 \text{ArCHO} \longrightarrow \text{Ar}-\text{CHOH}-\text{CO}-\text{Ar}$
Bimbaum-Simonini carboxylate-ester transformation	$2 \text{RCO}_2\text{M} \xrightarrow{(\text{X}_2)} \text{RCOOR}$

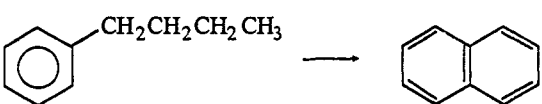
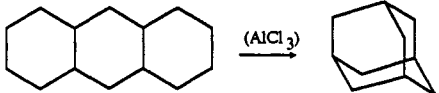
Name	Transformation
Borsche hydrazone-tetrahydroindole transformation	
Bucherer-Bergs hydantoin synthesis	$R-CO-R' \xrightarrow{(CO_2, NH_3, HCN)} \begin{array}{c} H \\   \\ R'-C-N \\   \quad // \\ R \quad O \\   \\ O \\   \\ NH \end{array}$
Cannizzaro aldehyde disproportionation	$2 ArCHO \longrightarrow ArCH_2OH + ArCO_2^-$ <p>(The separate transformations <math>ArCHO \longrightarrow ArCH_2OH</math> and <math>ArCHO \longrightarrow ArCO_2^-</math> have systematic names)</p>
Carbonyl-trithiane transformation	
Decker alkylpyridinium oxidation	
Demyanov ring contraction	
Demyanov ring expansion	
Diazoalkane-thiirane transformation	$2 R_2CN_2 \xrightarrow{(S)} \begin{array}{c} R_2C \quad CR_2 \\ \diagdown \quad / \\ S \end{array}$
Diazonium-arylhydrazine reduction	$ArN_2^+ \longrightarrow ArNHNH_2$
Diazotization	$RNH_2 \longrightarrow RN_2^+$ <p>(This could be named systematically, but obscurely, as the substitution of two hydrogens by =N<sup>+</sup>: azanyliumylidene-de-dihydro-bisubstitution)</p>
1,1-Dihaloalkene-alkyne transformation	$RCH=CX_2 \xrightarrow{(R'M)} R-C \equiv C-R'$
Di-π-methane rearrangement	
Eschenmoser-Tanabe ring cleavage	

Name	Transformation
Fischer indole synthesis	 $\text{C}_6\text{H}_5\text{NH-N}=\text{C}(\text{R})\text{CH}_2\text{R}' \longrightarrow \text{Indole}(\text{R}, \text{R}')$
Formaldehyde-hexamethylenetetramine transformation	$\text{CH}_2\text{O} \xrightarrow{(\text{NH}_3)} \text{Hexamethylenetetramine}$ 
Haloform-isocyanide transformation	$\text{CHX}_3 \xrightarrow{(\text{RNH}_2)} \text{C}^+\equiv\text{N}^-\text{R}$
Haloform reactions	$\begin{aligned} \text{CH}_3\text{CO-R} &\longrightarrow \text{CHX}_3 + \text{RCO}_2^- \\ \text{CH}_3\text{CHOH-R} &\longrightarrow \text{CHX}_3 + \text{RCO}_2^- \end{aligned}$
Hinsberg quinone-aryl sulfone transformation	 $\text{Quinone} \xrightarrow{(\text{ArSOOH})} \text{Sulfonated Hydroquinone}$
Hydrazine-azide transformation	$\text{RNHNH}_2 \longrightarrow \text{RN}_3$
Isocyanate-methylamine transformation	$\text{R-N=C=O} \longrightarrow \text{R-NH-CH}_3$
Isothiocyanate-methylamine transformation	$\text{R-N=C=S} \longrightarrow \text{R-NH-CH}_3$
Mark alkynol phosphate rearrangement	 $\text{R}^1\text{C}(\text{R}^2)\text{C}\equiv\text{C-R}^3 \text{ (with } \text{O-P} \text{ group)} \longrightarrow \text{R}^1\text{C}(\text{R}^2)=\text{C}=\text{C}(\text{R}^3)\text{ (with } \text{O-P} \text{ group)}$
Marker diosgenin degradation	
Mattox rearrangement	$\text{>C(OH)-CO-CH}_2\text{OH} \xrightarrow{(\text{HOAc})} \text{>C=C(OH)-CHO}$
Meyer-Schuster alkynol rearrangement	$\text{R-C}\equiv\text{C-CR}'_2\text{OH} \longrightarrow \text{R-CO-CH=CR}'_2$
Neber oxime tosylate-amino ketone rearrangement	$\text{R-CH}_2\text{-C(R')=N-OTos} \longrightarrow \text{R-CH(NH}_2\text{)-CO-R'}$
Nitro-azoxy reductive transformation	$2 \text{ArNO}_2 \longrightarrow \text{Ar-N}^+(\text{O})=\text{N}^-\text{Ar}$
<i>N</i> -Nitrosoamine-diazoalkane transformation	$\text{R}_2\text{CH-N(NO)-A} \longrightarrow \text{R}_2\text{C=N}^+=\text{N}^- \quad (\text{A} = \text{Tos, CONH}_2, \text{ etc})$


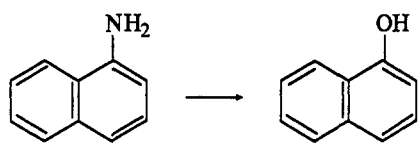
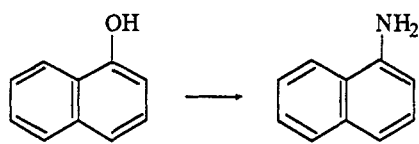


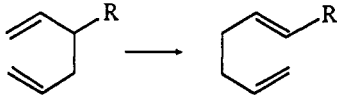
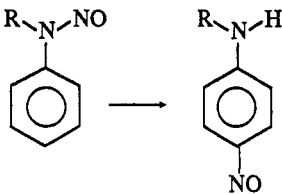
Name	Transformation
Oxa-di- $\pi$ -methane rearrangement	
Pearson hydrazone-amide rearrangement	$\text{R}-\underset{\text{R}'}{\text{C}}=\text{N}-\text{NH}_2 \xrightarrow{(\text{HONO})} \text{R}-\text{CO}-\text{NH}-\text{R}'$
Piloty-Robinson pyrrole synthesis	$\text{RCH}_2-\underset{\text{R}'}{\text{C}}=\text{N}-\text{N}=\underset{\text{R}'}{\text{C}}-\text{CH}_2\text{R} \longrightarrow \begin{array}{c} \text{H} \\   \\ \text{R}'-\text{C}_5\text{H}_3-\text{N}-\text{C}_5\text{H}_3-\text{R}' \\   \\ \text{R} \end{array}$
Porter-Silber ketose-hydrazone rearrangement	$>\text{C}(\text{OH})-\text{CO}-\text{CH}_2\text{OH} \xrightarrow{(\text{ArNHNH}_2)} >\text{CH}-\text{CO}-\text{CH}=\text{N}-\text{NHAr}$
Pummerer methyl sulfoxide rearrangement	$\text{R}-\text{SO}-\text{CH}_3 \longrightarrow \text{R}-\text{S}-\text{CH}_2-\text{OAc}$
Ramberg-Bäcklund halosulfone transformation	$\text{R}-\underset{ }{\text{CH}}-\text{SO}_2-\underset{ }{\text{CX}}-\text{R}' \longrightarrow \text{R}-\underset{ }{\text{C}}=\underset{ }{\text{C}}-\text{R}'$
Reddelien pyridine synthesis	$\text{PhCOCH}_3 \xrightarrow{(\text{PhCH}_2\text{NH}_2)} \begin{array}{c} \text{Ph} \\   \\ \text{C}_5\text{H}_3-\text{N}-\text{C}_5\text{H}_3 \\   \\ \text{Ph} \end{array}$
Reductive azoxy cleavage	$\text{Ar}-\overset{+}{\text{N}}(\text{O}^-)=\text{N}-\text{Ar} \longrightarrow 2 \text{ArNH}_2$
Secoalkylation (overall transformation)	
Serini acetoxyalcohol-carbonyl transformation	$>\text{C}(\text{OH})-\text{CH}(\text{OAc})- \longrightarrow >\text{CH}-\text{CO}-$
Sulfonic acid-thiol reduction	$\text{RSO}_2\text{OH} \longrightarrow \text{RSH}$
Thiol-sulfonic acid oxidation	$\text{RSH} \longrightarrow \text{RSO}_2\text{OH}$
Thiol-sulfonyl halide oxidation	$\text{RSH} \longrightarrow \text{RSO}_2\text{X}$
Tiemann amidoxime-urea rearrangement	$\text{R}-\underset{\text{N-OA}}{\text{C}}-\text{NH}_2 \longrightarrow \text{R}-\text{NH}-\text{CO}-\text{NH}_2 \quad (\text{A} = \text{H} \text{ or } \text{Tos})$
Tishchenko aldehyde-ester disproportionation	$2 \text{RCHO} \longrightarrow \text{RCOOCH}_2\text{R}$
Varrentrapp cleavage	$\text{RCH}=\text{CH}-(\text{CH}_2)_n-\text{CO}_2^- \longrightarrow \text{R}(\text{CH}_2)_n-\text{CO}_2^- + \text{CH}_3\text{CO}_2^-$
Von Auwers coumaranone-chromone rearrangement	

## Families of closely related transformations

Alkene metathesis	$2 \begin{array}{c} R^1 \quad R^3 \\ \diagdown \quad / \\ C=C \\ / \quad \diagdown \\ R^2 \quad R^4 \end{array} \longrightarrow \begin{array}{c} R^1 \quad R^1 \\ \diagdown \quad / \\ C=C \\ / \quad \diagdown \\ R^2 \quad R^2 \end{array} + \begin{array}{c} R^3 \quad R^3 \\ \diagdown \quad / \\ C=C \\ / \quad \diagdown \\ R^4 \quad R^4 \end{array}$
Cycloalkanone oxidative ring opening	$\begin{array}{c} \text{Cyclohexanone} \\ \text{Cyclohexanone} \end{array} \longrightarrow \text{HOCO}-(\text{CH}_2)_4-\text{COOH}$ <p>(Other transformations of the same type may give keto acids and diketones as products)</p>
Cyclodehydrogenation (This name includes all transformations in which an aliphatic chain is cyclized to give an aromatic ring, whether or not the original chain is attached to an aromatic ring)	 <p>Reaction of 1-(4-phenylbutyl)benzene to fluorene.</p>
Schleyer adamantization (This name includes all cases in which a polycyclic system is isomerized to an adamantane derivative)	 <p>Reaction of tricyclo[3.3.1]nonane to adamantane, catalyzed by <math>\text{AlCl}_3</math>.</p>
Willgerodt carbonyl transformation	$\text{ArCOCH}_3 \longrightarrow \text{ArCONH}_2 \text{ or } \text{ArCH}_2\text{CO}_2^-$

## Appendix Transformations accomplished by some name reactions

Common name	Systematic name	Transformation
Aldol reaction, Claisen-Schmidt reaction	<i>O</i> -hydro, <i>C</i> -[1-acylalkyl]-addition or 1-acylalkylidene-de-oxo- bisubstitution	$\text{R}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{R}' \xrightarrow{>\text{CH}-\text{CO}-\text{R}''} \begin{array}{c} -\text{C}-\text{CO}-\text{R}'' \\   \\ \text{R}-\text{C}-\text{R}' \\   \\ \text{OH} \end{array} \text{ or } \begin{array}{c} -\text{CH}-\text{CO}-\text{R}'' \\    \\ \text{R}-\text{C}-\text{R}' \end{array}$
Benzilic acid rearrangement	1/ <i>O</i> -hydro, 3/oxido-(1/ $\rightarrow$ 2/aryl)- <i>migro</i> -addition	$\text{Ar}-\text{CO}-\text{CO}-\text{Ar} \longrightarrow \text{Ar}_2\text{C}(\text{OH})\text{CO}_2^-$
Birch reduction	1/4/dihydro-addition	 <p>Reaction of benzene to 1,4-cyclohexadiene.</p>
Bucherer reaction (1)	hydroxy-de-amination	 <p>Reaction of 1-aminonaphthalene to 1-hydroxynaphthalene.</p>
Bucherer reaction (2)	amino-de-hydroxylation	 <p>Reaction of 1-hydroxynaphthalene to 1-aminonaphthalene.</p>

Common name	Systematic name	Transformation
Claisen condensation	[1-(alkoxycarbonyl)alkyl]- de-alkoxylation and acylation (acyl-de-hydrogenation)	$RCH_2-COOR' \xrightarrow{(R'O^-)} RCH_2-CO-CHR-COOR'$
Clemmensen reduction, Mozingo reduction, Wolff-Kishner reduction	dihydro-de-oxo-bisubstitution	$R_2C=O \rightarrow R_2CH_2$
Cope rearrangement	(3/4/) $\rightarrow$ (1/6/)- <i>sigma</i> -migration or [3,3] <i>sigma</i> -migration	
Delépine reaction	amino-de-chlorination	$RCl \xrightarrow{((CH_2)_6N_4)} RNH_2$
Finkelstein reaction	halo-de-halogenation	$R-Hal \rightarrow R-Hal'$
Fischer-Hepp rearrangement	1/C-hydro,5/N-nitroso-interchange	
Friedel-Crafts acylation	acylation, acyl-de-hydrogenation aryl-de-chlorination	$ArH \rightarrow ArCOR$ $RCOCl \rightarrow ArCOR$
Friedel-Crafts alkylation (1)	alkylation, alkyl-de-hydrogenation aryl-de-chlorination	$ArH \rightarrow ArR$ $RCl \rightarrow ArR$
Friedel-Crafts alkylation (2)	alkylation or alkyl-de-hydrogenation hydro,aryl-addition	$ArH \xrightarrow{(>C=C<)} >CH-CAr<$ $>C=C< \xrightarrow{(ArH)} >CH-CAr<$
Haller-Bauer reaction	amino-de-alkylation and hydro-de-acylation	$R-CO-R' \rightarrow R-CO-NH_2 + R'H$
Hell-Volhard-Zelinskii reaction	halogenation, halo-de-hydrogenation	$R-CH_2-COOH \rightarrow R-CHHal-COOH$
Hofmann degradation	hydro-trialkylammonio-elimination	$>CH-CNR_3^+ \rightarrow >C=C<$
Hofmann rearrangement	bishydrogen-(2/ $\rightarrow$ 1/N-alkyl)- <i>migro</i> -detachment	$RCONH_2 \rightarrow R-N=C=O$
Japp-Klingemann reaction (1)	arylhrazono-de-hydro,carboxy- bisubstitution	$RCO-CHR'-COOH \xrightarrow{(ArN_2^+)} RCO-CR'=N-NHAr$
Japp-Klingemann reaction (2)	arylhrazono-de-hydro,acyl- bisubstitution	$RCO-CHR'-COR'' \xrightarrow{(ArN_2^+)} RCO-CR'=N-NHAr$
Kolbe-Schmitt reaction	carboxylation or carboxy-de-hydrogenation	$ArH \rightarrow ArCOOH$
Kucherov reaction	dihydro-oxo-biaddition	$-C=C- \rightarrow -CO-CH_2-$
McFadyen-Stevens reaction	hydro-de-tosylhydrazino- substitution	$RCONHNHTos \rightarrow RCHO$
Meerwein-Ponndorf-Verley reduction	O, C-dihydro-addition	$>C=O \xrightarrow{(Me_2CHOH)} >CH-OH$
Menshutkin reaction	trialkylammonio-de-halogenation	$RHal \xrightarrow{(R'_3N)} RR'_3N^+ Hal^-$

Common name	Systematic name	Transformation
Michael reaction (one example)	hydro,bis(ethoxycarbonyl)methyl- addition	$>C=C-CO-R \xrightarrow{(CH_2(COOEt)_2)} \begin{array}{c} H \\   \\ -C-C-CO-R \\   \\ CH(COOEt)_2 \end{array}$
Nenitzescu acylation	hydro,acyl-addition	$>C=C < \longrightarrow >CH-C(COR)<$
Oppenauer oxidation	O,C-dihydro-elimination	$>CH-OH \xrightarrow[Al(O-t-Bu)_3]{(R_2CO)} >C=O$
Paterno-Büchi reaction	OC,CC-cyclo-[alkane-1/2/diyl]- 1/2/addition	$R-CO-R' \xrightarrow[h\nu]{>C=C} \begin{array}{c} R \\   \\ \square \\   \\ O \end{array} R'$
	OC,CC-cyclo-[1/oxyalkyl]- 1/2/addition	$>C=C < \xrightarrow[h\nu]{(R-CO-R')} \begin{array}{c} R \\   \\ \square \\   \\ O \end{array} R'$
Prevost reaction, Woodward reaction	dihydroxy-addition	$>C=C < \longrightarrow -C(OH)-C(OH)-$
Prilezhaev reaction	epi-oxygen-addition	$>C=C < \longrightarrow \begin{array}{c}   \quad   \\ \backslash \quad / \\ C \quad C \\ / \quad \backslash \\ O \end{array}$
Radziszewski reaction	N,N-dihydro-C-oxo-biaddition	$RCN \longrightarrow RCONH_2$
Reformatsky reaction	O-hydro-C-[1-ethoxycarbonylalkyl]- addition	$R_2CO \xrightarrow[Zn]{(R'_2CBrCOOEt)} R_2C(OH)-CR'_2COOEt$
	[1-hydroxyalkyl]-de-halogenation	$R'_2CBrCOOEt \xrightarrow[Zn]{(R_2CO)} R_2C(OH)-CR'_2COOEt$
Ritter reaction	N-hydro,N-alkyl-C-oxo-biaddition	$RCN \xrightarrow{(R'OH)} R-CO-NH-R'$
	acylamino-de-hydroxylation	$R'OH \xrightarrow{(RCN)} R-CO-NH-R'$
Sandmeyer reaction (1)	chloro-de-diazonation	$ArN_2^+ \longrightarrow ArCl$
	bromo-de-diazonation	$ArN_2^+ \longrightarrow ArBr$
Sandmeyer reaction (2)	cyano-de-diazonation	$ArN_2^+ \longrightarrow ArCN$
Schmidt reaction (of ketones)	imino-insertion	$R-CO-R' \xrightarrow[(HN_3)]{(H^+)} R-CO-NH-R'$
Ullmann reaction	de-halogen-coupling	$2 ArHal \longrightarrow Ar-Ar$

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