

# INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ORGANIC CHEMISTRY DIVISION  
COMMISSION ON PHYSICAL ORGANIC CHEMISTRY\*

## THE DETAILED LINEAR REPRESENTATION OF REACTION MECHANISMS

(Recommendations 1988)

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# The detailed linear representation of reaction mechanisms (Recommendations 1988)

Abstract - These rules describe a system for the representation of models of reaction mechanisms in a linear form, using standard computer characters. A model of the reaction mechanism is described in a sufficiently detailed manner that most of the important features can be represented, and the notation can be related to the conventional diagrammatic representation of reaction mechanisms. The detail given is however such that it is not intended that the representation should be used in speech. The model is described primarily in terms of bond making and bond breaking steps, but the representation allows the encoding of much other information. It allows the representation of single reaction steps or reaction sequences, and should specify exactly how the reagents are converted into the products. It is primarily designed for thermal organic reactions, but is not in principle limited to that field.

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## PREAMBLE

These rules constitute a system for the linear representation of models of reaction mechanisms in a form sufficiently detailed to enable most of the salient facts about the model of an actual reaction to be represented in a way suitable both for conversion into and derivation from conventional diagrammatic form, yet suitable for computer storage and retrieval. It should be emphasised that the representation is of a model; at no point does the use of a particular example imply that we advocate that a particular model is a correct representation of the mechanism of the example reaction. The representation is based on the concept of bond-making and bond-breaking steps<sup>1</sup> but is constructed in a way which allows extension to other types of transition state, the inclusion of detailed positional information, and the addition of "extra-kinetic" information applicable both to an individual elementary reaction and to a reaction sequence. It has been developed from a previous scheme,<sup>2</sup> and where possible, brought into compatibility with the proposals for the symbolization of simple reactions.<sup>3</sup> It must be emphasised that the latter scheme is confined to the derivation of simple speech/writing names, while the present is intended to be a detailed representation, primarily intended for computer filing and indexing.

The basic conceptual unit is the "primitive change" ("PC") as defined in the Glossary<sup>4</sup> and Section 1 is concerned with the identification and representation of the primitive changes. These are not limited to the obvious areas of bond formation (association) or bond breakage (dissociation) though these particular primitive changes provide many of the most commonly used units in reaction models, and in principle the rules should be applicable to any reaction model which is based on discrete bond changes. There is no restriction to reactions involving carbon atoms. Some attempt has been made to indicate conformational, spectroscopic, and spin changes, and this could be further extended, leading into the fields of photochemistry, surface chemistry, or electrochemistry. In some cases (e.g. various photochemical or excited state processes) it would be necessary to define new PC's before the models could be adequately represented. No attempt is made to represent rehybridisation details. Primitive changes are designated by one letter or a group of letters, preferably having some mnemonic value. Changes of the same general type begin with the same capital letter (e.g. A for Association between two atomic centres) modified by lower case letters indicating subdivisions of the group (e.g. c for colligative). The atoms on which the change operates are listed in a specified order in the parentheses following the change designator. The notation is analogous to that used for mathematical functions. The rules to be followed are in Section 1. It must be emphasised that the list of PC's hereafter defined is not to be regarded as complete; new ones can be added as necessary to accommodate new mechanistic insights.

Elementary reactions<sup>4</sup> can be regarded as being built up from one or more primitive changes, and a reaction mechanism consists of one or more elementary reactions which occur sequentially or in competition acting on one or more reagent species. Section 2 details the rules by which primitive change representations may be combined to build up a complete notation for an elementary reaction.

To write down an elementary reaction in general the constituent primitive changes are written in line (Rule 2.1) and two sequential elementary reactions are joined with a "+" sign (Rule 2.2). The rest of section 2 deals with the addition of extra information, often optional, which is relevant only at the level of the elementary reaction or reaction sequence, and hence is written as a suffix to the elementary reaction notation. This may include information on the sequence of reactions, stereochemistry, and spin multiplicity changes, and non-thermodynamic information on rate limiting steps or diffusion control, and further information could be added as required. At present no attempt has been made to define a set of symbols to convey stereochemical information.

When a mechanism is considered it is applied to a specific substrate or group of substrates. It is therefore necessary to add to the list of atoms in the primitive change representation indications as to relative site in a molecule, or even as to which of several molecules is involved. Section 3 addresses these problems. Rule 3.1 defines positional indicators within the reaction centre. Rule 3.2 indicates how to name such centres, and Rule 3.3 shows how to distinguish between different molecules. The rest of Section 3 deals with specific problems involving electron transfer, proton transfer, and delocalised bonding.

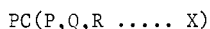
Section 4 gives further examples in addition to those used to illustrate the individual rules, and section 5 provides a table of the symbols used and an index to the rule concerned with each. Section 6 provides a comparison with Ingold-type symbols and with ref.3 in tabular form.

The abbreviations PC for "primitive change" and ER for "elementary reaction" are used in the text below. It is occasionally necessary when illustrating one rule, to use a symbol not defined until later in the document; the reader should be able to locate all key definitions via the table in section 5.

## SECTION 1. REPRESENTATIONS OF PRIMITIVE CHANGES

### Rule 1.1 general representation

The primitive change (PC) is represented in functional notation as



where PC defines the operation which takes place on the assembly of atoms P to X. The detailed form of the atom representation, here represented in generalised form, will be defined later (Section 3). Representations of operand atoms are separated by commas. Information on electron involvement, where relevant is added in square brackets [ ] - see Rule 1.10 below. If more than one molecule is involved each is referred to by a numeral in a pointed bracket, e.g. <2> (Section 3.3).

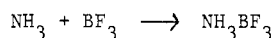
Note. Where the PC is a bond forming or breaking operator there will normally be only two operand atoms concerned, but if the PC represents a multi-centre process then more than two atoms may be specified as operands. Likewise if the PC does not represent loss or gain of conventional bonds there is no restriction as to the number of atoms specified, but the definition of a particular PC must be explicit as to the number of operands it requires. It may be convenient to define compound PC's for a small number of processes for which full representation may be over-elaborate (e.g. rule 1.10).

### Rule 1.2 $\sigma$ -bond formation

Formation of a single covalent bond of  $\sigma$  symmetry is represented as follows using symbols beginning with the capital letter "A".

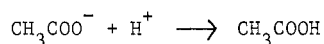
RULE 1.2.1 A(P,Q) - A coordination where P is the atom providing the electron pair. Both P and Q are electron paired species. Only one two-centre bond is formed.

Example 1.2.1.1



A(N,B)

Example 1.2.1.2

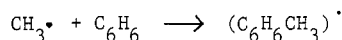


A(O,H)

See also examples 1.5.1

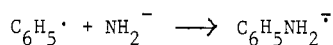
**RULE 1.2.2** Ar(P,Q) - A bond formation process between an electron paired species and a radical. The common case is that P provides an electron pair while Q is a radical. In the less common case where the electron paired species is electron deficient (e.g.  $R_3C^+$ ), P shall represent the radical and Q the other reagent. The letter "r" indicates the radical character of both a reactant and the products. See also examples 4.1 and 4.3.

Example 1.2.2.1



Ar(C,C)

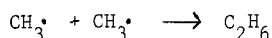
Example 1.2.2.2 - one step of the " $S_{RN}1$ " process



Ar(N,C)

**RULE 1.2.3** Ac(P,Q) - A bond formation where both P and Q are radicals (c = colligation). The lower Cahn-Ingold-Prelog (C.I.P.)<sup>5</sup> priority group should be written as P.

Example 1.2.3



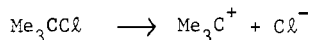
Ac(C,C)

### Rule 1.3 $\sigma$ -bond breakage

Breakage of a single covalent bond of  $\sigma$  symmetry (the converse of rule 1.2) is represented by PC symbols beginning with letter "D".

**RULE 1.3.1** D(P,Q) - Heterolytic dissociation, the reverse of A(P,Q), in which the electron pair is retained by P.

Example 1.3.1.1

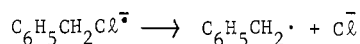


D(Cl,C)

See also examples 1.4.1.1 etc.

**RULE 1.3.2** Dr(P,Q) - Dissociation of a radical species. This is the reverse of Ar(P,Q). In the usual case the atom P retains the electron pair and Q is a radical, or if the electron paired product is electron deficient it is Q while the radical is P.

Example 1.3.2.1 - The dissociation step in the " $S_{RN}1$ " process.

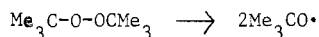


Dr(Cl,C)

See also examples 1.4.3, 1.5.2, 4.1

**RULE 1.3.3** Dc(P,Q) - The reverse of 1.2.3, i.e. homolytic fission of an electron paired  $\sigma$  bond; both products P and Q are radicals. P should have a lower or identical priority to Q, as defined by the C.I.P. rules.

Example 1.3.3.1



Dc(O,O)

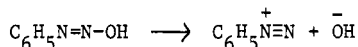
If it should be useful to specify the spin state of the product radical pair the symbol "Dc" could be extended (see Rule 2.7).

**Rule 1.4  $\pi$ -bond formation**

Formation of a single covalent bond of  $\pi$  symmetry uses Ap, with "p" to indicate  $\pi$  character.

RULE 1.4.1 Ap(P,Q) - Heterolytic  $\pi$  bond formation. The order of P and Q is defined as in 1.2.1.

Example 1.4.1.1



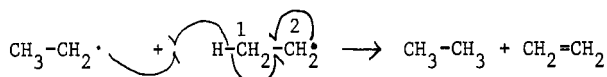
Ap(N,N) D(O,N)

**Note.** Here, and in most  $\pi$ -bond reactions, it is difficult to find examples in which a single PC can exist in isolation as an elementary reaction (ER). An appropriate  $\sigma$ -bond PC should therefore accompany all  $\pi$ -bond changes. The sequence in which the two PC's are combined is defined in section 2; the dissociative PC is an example of rule 1.3.1.

RULE 1.4.2 Apr(P,Q) - One atom usually Q, provides an odd electron, the sequence of P and Q is as in 1.2.2, of which this process is the  $\pi$ -bond analog.

RULE 1.4.3 Apc(P,Q) - Both atoms provide odd electrons - the  $\pi$ -analog of 1.2.3.

Example 1.4.3.1



Ar(H,C<1>) Dr(H,C<2>) Apc(2/C,C)

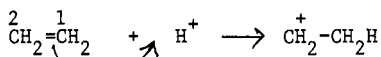
Section 3 gives full details of the significance of the numbers in < > and before /. Briefly "n/" refers to the atom numbered "n" in the diagram while <m> refers to the m<sup>th</sup> reagent molecule drawn.

**Rule 1.5  $\pi$ -bond breakage**

Breaking of a single covalent bond of  $\pi$  symmetry uses "Dp".

RULE 1.5.1 Dp(P,Q) - (c.f. 1.3.1) Heterolytic fission of a  $\pi$  bond.

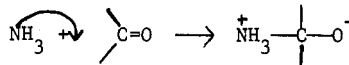
Example 1.5.1.1



Dp(C,2/C) A(C,H)

and the reverse process is written D(C,H) Ap(C,2/C)

Example 1.5.1.2



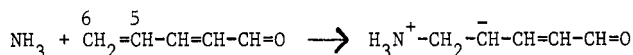
A(N,C) Dp(O,C)

and its reverse is written Ap(O,C) D(N,C)

**Note.** In both Rules 1.4 and 1.5 the same rules apply as in 1.2 and 1.3 as to the placement of electron pairs or spin; the representation of  $\pi$  bond changes is independent of any concurrent  $\sigma$  bond changes between the same atoms (see rule 2.1.2).

Formation of a single covalent bond of  $\sigma$  symmetry to one end of a  $\pi$  system is represented as in 1.5.1 above. In the case where a single  $\pi$  bond is involved the change in the  $\pi$  bond is specified; this clearly distinguishes the process from that represented by the simple association in examples 1.2.1. If the addition is to the end of an extended  $\pi$  system, and it is not necessary to specify the extent of the consequential  $\pi$  bond changes the symbol "\$" should be suffixed to the ER to indicate that the formation of only one canonical form has been specified (see rule 3.4.3).

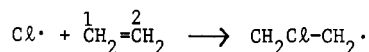
Example 1.5.1.3



A(N,6/C) Dp(5/C,6/C):\$

**RULE 1.5.2** Dpr(P,Q) - (c.f. 1.3.2) Homolytic dissociation of  $\pi$  bond to a radical and an electron paired product. The precursor is necessarily a radical, and the fragment carrying the spin is normally Q (c.f. 1.3.2).

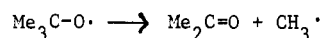
Example 1.5.2.1



Ar(C,C $\ell$ ) Dpr(C,2/C)

and the reverse process Apr(C,2/C) Dr(C,C $\ell$ )

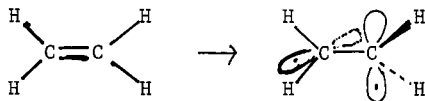
Example 1.5.2.2



Apr(C,O) Dr(C,2/C)

**RULE 1.5.3** Dpc(P,Q) - (c.f. 1.3.3) Homolytic dissociation of a  $\pi$  bond to give two unpaired electrons. P should have a lower C.I.P. priority than Q.

Example 1.5.3.1



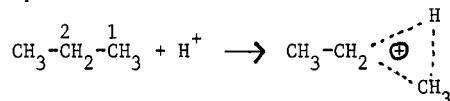
Dpc(C,C)

### Rule 1.6 three centre bonds

There are a number of primitive changes which can only be dissected into two-atom interactions in a very artificial manner. The use of A and D symbols as above is to be avoided for these since they are implicitly associated with two-centre bond changes. The symbol "U" (= union) is adopted for 3-centre bonds, with "V" as its reverse.

**RULE 1.6.1** U(P,Q,R) - Represents the formation of a three centre bond by attack of an electrophile (R) on a  $\sigma$  bond P-Q.

Example 1.6.1.1



U(C,2/C,H)

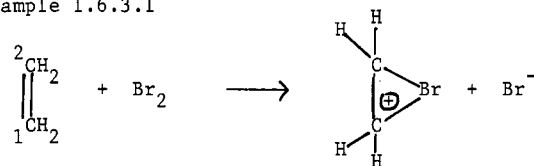
**RULE 1.6.2** V(P,Q,R) - Dissociation of a three centre complex leaving P and Q  $\sigma$  bonded, with R electron deficient.

Example 1.6.2.1 the reverse of 1.6.1.1

V(C,2/C,H)

**RULE 1.6.3** Up(P,Q,R) - Formation of an adduct from atoms P,Q (providing electrons from a  $\pi$  bond) to R.

Example 1.6.3.1



Up(C,2/C,Br) D(Br,Br)

**Note.** Weaker associations (e.g. between molecular  $\text{Br}_2$  and an aromatic compound) can be represented as in Rule 1.9. See example 1.9.2.2.

**RULE 1.6.4** Vp(P,Q,R) - The reverse of the process described in 1.6.3, i.e. dissociation of a  $\pi$  adduct, where P,Q eventually are  $\pi$  bonded, and R is the electrophile which has left.

Example 1.6.4.1 - the reverse of example 1.6.3.1

A(Br,Br) Vp(C,2/C,Br)

**Note.** This form of representation could be expanded to allow for  $\pi$  bonds from more than two centres, the numeral indicating the number of centres, each being specified.

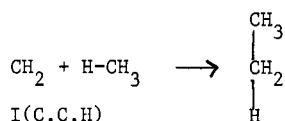
e.g. Up3(C,2/C,3/C,M) for the formation of an allylic  $\pi$  bond to a metal, M.

**Rule 1.7 insertions and extrusions**

"I" is the symbol for insertion, with "X" for the reverse.

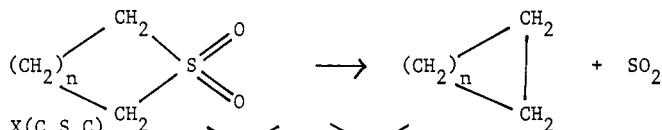
**RULE 1.7.1** I(P,Q,R) - Insertion of Q into the  $\sigma$  bond P,R.

Example 1.7.1.1



**RULE 1.7.2** X(P,Q,R) - Extrusion (the reverse of insertion) of Q from between P and R which then form a sigma bond.

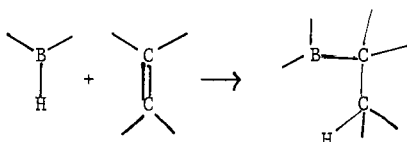
Example 1.7.2.1



**Note.** Insertion into a  $\pi$  bond (e.g.  $\text{CH}_2 + \text{C}=\text{O} \longrightarrow \text{C}(\text{O})-\text{CH}_2$ ) and its reverse are treated as a special case of cheletropic electrocyclic addition and its reverse, see examples 1.10.1.5 and 1.10.2.2 below.

**RULE 1.7.3** Ia(P,Q,R,S) - An insertion process in which the inserting reagent provides two adjacent atoms to the product. The inserting reagent is Q-R and bonds are formed between P and Q and between R and S.

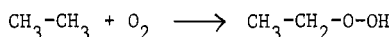
Example 1.7.3.1 - insertion of a C=C into a B-H bond



Ia(B,C,2/C,H)

**Note.** This reaction can be considered as having a pericyclic reaction mechanism (see example 1.10.8.2).

Example 1.7.3.2 - insertion of  $\text{O}_2$  into a C-H bond



Ia(C,O,O,H)

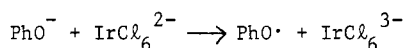
**RULE 1.7.4** Xa(P,Q,R,S) - An extrusion process which extrudes two adjacent atoms Q,R from between P and S (the reverse of 1.7.3).

**Rule 1.8 electron transfer**

The symbol T is reserved for electron transfer of various types.

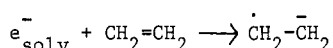
**RULE 1.8.1** T(S,R) - Represents transfer of a single electron from the source S to the recipient R. If necessary the source and recipient may be designated by orbital designation rather than just the element symbol, and this symbol will therefore suffice for both inter- and intramolecular electron transfer. If the source of recipient is general, or if it is not necessary to specify it, the symbol Q can be used; (eg, es, ec) may be used for free or solvated electrons. See Rules 3.4.1, 3.4.2. A modified T symbol could be used to indicate radiative energy transfer associated with electron transfer.

Example 1.8.1.1



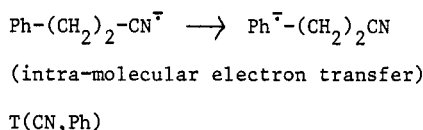
T(O,Ir)

Example 1.8.1.2

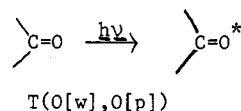


T(es,C)

## Example 1.8.1.3

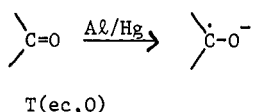


## Example 1.8.1.4



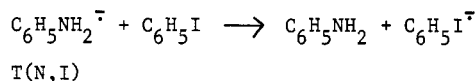
(see Rule 1.10 for the designation of electron types, w = nonbonded, p =  $\pi$ ).

## Example 1.8.1.5



## Example 1.8.1.6

the electron transfer step of the "S<sub>RN</sub>1" process.

**Rule 1.9 weak associations**

Elementary reactions may involve the formation and dissociation of entities held together by weaker forces than the normal covalent bond, e.g. ion pair attraction or hydrogen bonding. Such processes are normally rate-limited by diffusion. It may be difficult to specify unambiguously the primitive changes involved in such reactions and therefore the generic symbol "C" (for diffusional combination) will be used, with Cw for a second (weaker) level of association if in a reaction two such levels of weak association need to be distinguished, e.g. both "intimate" and "solvent separated" ion pairs. If two atoms first associate weakly, then form a covalent bond (i.e. two separate elementary reactions) the covalent bond formation step is assumed to start from the weakly associated intermediate; similarly a covalent dissociation is assumed to result in free fragments unless a subsequent elementary process is written specifying the dissociation of (say) an ion pair. This dissociation, the reverse of C, is called P (Parting).

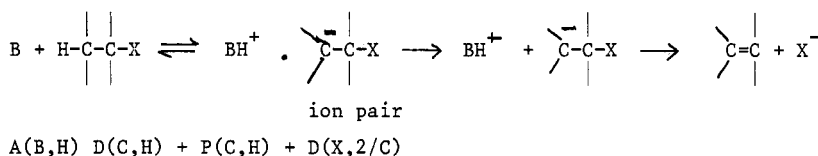
RULE 1.9.1 C(P,Q) - The formation of a weak association between P and Q

Cw(P,Q) - The formation of a very weak association

RULE 1.9.2 P(P,Q) - Dissociation of a weakly bound adduct of P and Q

Pw(P,Q) - Dissociation of a very weakly bound adduct

## Example 1.9.2.1 - Elimination via an ion pair



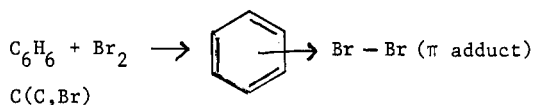
If the ion pair does not have time to dissociate before the carbanion splits, the P step does not happen and is omitted, the close linking of the processes being symbolised by "\*" (Rule 2.2),

i.e. A(B,H) D(C,H) \* D(X,2/C)

while the P step will also be omitted if the dissociation of the ion pair is not kinetically significant (i.e. as is commonly the case, it is complete before the carbanion is lost):-

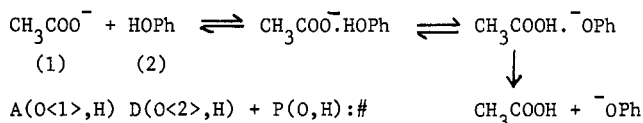
A(B,H) D(C,H) + D(X,2/C)

## Example 1.9.2.2



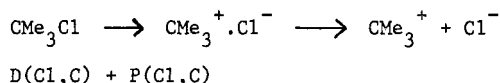
The C primitive change has two parameters: in the above case one might wish to write a reaction model which explicitly indicates that more than one carbon atom is involved. As this multiple association is related to the delocalised nature of the reagent, the symbol \$ can be appended (see rule 3.4.3) viz. C(C,Br):\$. If both Br atoms are bonded to the ring a further PC is needed.

## Example 1.9.2.3 - Rate limiting separation of the products of a thermodynamically unfavourable proton transfer.





It should be noted that weak associations between reagents before a reaction or between products after are not specified unless they are mechanistically significant. Thus if ion pair formation for a heterolytic dissociation needs to be specified, example 1.3.1.1 (solvolysis of  $\text{CMe}_3\text{Cl}$ ) becomes example 1.9.2.4:-

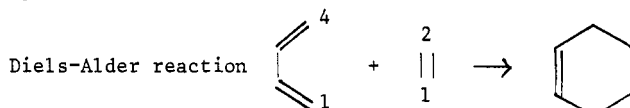


### Rule 1.10 pericyclic processes

**Pericyclic reactions.** While it is possible to devise sequences of the above symbols which can represent pericyclic reactions, and by introduction of arbitrary rules it is possible to obtain unique representations, it is better to define specific multicentre primitive changes. As full covalent bonds are usually formed and broken the A and D symbols are used, with the suffix "cy" to indicate the concerted cyclic nature of the electron shifts. A single primitive change cannot of course represent a stepwise reaction. The atoms are indicated in pairs in the same sequence as the A and D symbols. The sequence in which the atom symbols are written is the same as the sequence of atoms around the electrocycle. If there is a choice the atom with the lowest relative positional number in the minimum structures is specified first; if ambiguity still exists then the first atom written should have lower C.I.P. priority than the second. See Rule 1.10.8 for the rules for selecting the PC representation for various electrocyclic processes. There are essentially four common types of pericyclic reactions.

**RULE 1.10.1** AAcy(P,Q,R,S) [n] - Cycloadditions in which two new  $\sigma$  bonds are formed, with P forming a bond to Q and R to S, P and S being in one molecule and Q with R in the second. The portion within the [ ] is the optional description of their stereoelectronic nature by the designation of the orbitals involved in conventional manner except that no subscripts or Greek letters can be used. Thus use p for  $\pi$ , s for  $\sigma$ , and w for  $\omega$  (omega), with symbols for s (suprafacial) and a (antarafacial), on the line.<sup>6</sup> An arabic numeral gives the number of electrons involved.

Example 1.10.1.1

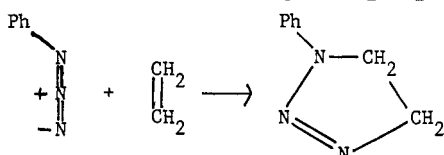


AAcy(C,C,4/C,2/C) [p4s + p2s]

Here atoms P and Q are both C, but are not identical since they must be in different molecules.

Example 1.10.1.2

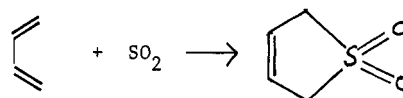
Dipolar addition of  $\Phi\text{-N}_3$  to  $\text{CH}_2=\text{CH}_2$



AAcy(C,N,3/N,2/C) [p4s + p2s]

Example 1.10.1.3

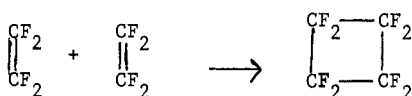
Cheletropic addition of



AAcy(C,S,S,4/C) [p4s + w2]

Note that the cheletropic nature is shown by use of the same atom twice: the AAcy PC is defined as always having four operands. In this case atoms Q and R in the definition, which must be in the same molecule, happen to be identical.

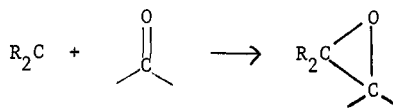
Example 1.10.1.4



(a "forbidden" process)

AAcy(C,C,2/C,2/C) [p2s + p2s]

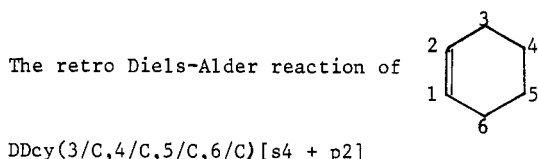
Example 1.10.1.5 - Carbene addition to  $\text{C}=\text{O}$



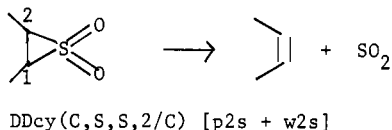
AAcy(C,C<2>,O,C)

RULE 1.10.2 DDcy(P,Q,R,S) [n + m] - P separates from Q, R from S, and P and S finish up in one fragment Q,R in the other.

Example 1.10.2.1



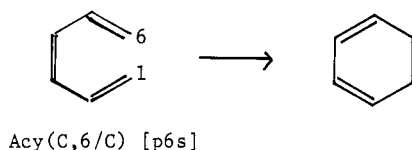
Example 1.10.2.2



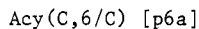
Cheletropic nature is again shown by S appearing twice.

RULE 1.10.3 Acy(P,Q) [n] - An electrocyclic reaction involving n electrons in which atoms P and Q become bonded. The atom with the lower locant is written first (see above).

Example 1.10.3.1

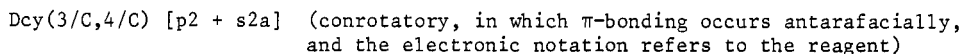
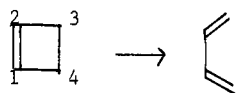


As bonding between atoms 1 and 6 occurs on the same face of the molecule in the allowed (disrotatory) reaction s (suprafacial) is used. The corresponding thermally forbidden reaction is

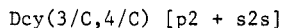


RULE 1.10.4 Dcy(P,Q) [n] - Electrocyclic ring opening, the converse of rule 1.10.3. The necessary  $\pi$  bond switches are implied by the value of "n". The atom with the lower locant is written first.

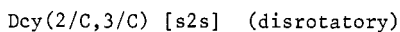
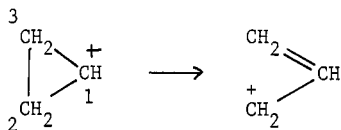
Example 1.10.4.1



The corresponding forbidden reaction would be

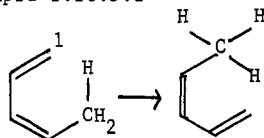


Example 1.10.4.2



**RULE 1.10.5** ADcy(P,Q,R,S) [n] - A sigmatropic reaction in which P bonds to Q while R breaks from S, and n is the number and type of electrons involved. Note that the conventional [i,j] notation for the relative positions of the atoms P,Q,R,S is not needed if the notation clearly identifies P,Q,R and S and that the electronic notation used does not involve commas but + signs if several orbitals are specified, so avoiding confusion with the [i,j] notation. The atom with the lowest locant is written first.

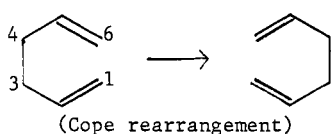
Example 1.10.5.1



ADcy(C,H,H,5/C) [6s] (6-electrons, suprafacial)

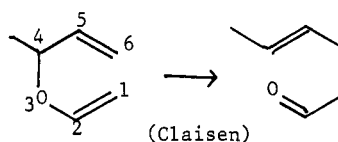
The [1,5] nature is shown by the same atom being designated for Q and R while P and S are 5 apart.

Example 1.10.5.2



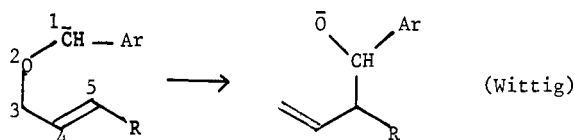
ADcy(C,6/C,4/C,3/C) [p2 + s2 + p2]

Example 1.10.5.3



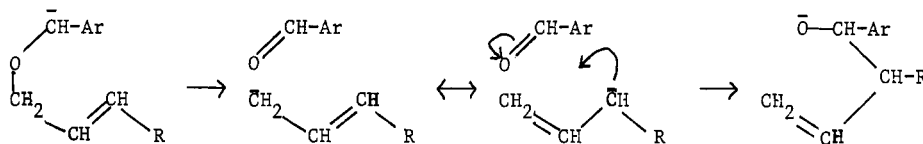
ADcy(C,6/C,4/C,O) [p2 + s2 + p2]

Example 1.10.5.4



ADcy(C,5/C,3/C,O) [6] (described as a [2,3] sigmatropic reaction)

Example 1.10.5.5 - The above reaction can be accounted for by a two-step ionic mechanism which provides a different mechanistic model:

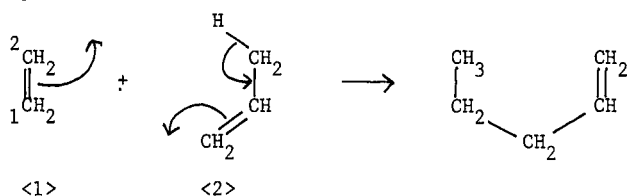


Ap(C,O) D(3/C,O) Ap(3/C,4/C) Dp(5/C,4/C):\$

+ A(5/C,C) Dp(O,C)

**RULE 1.10.6** ADAcy(P,Q,R,S,T,U) [n] - This is the "ene" reaction where two connections are formed and one broken. Again the atoms specified are in the same sequence as the initial A's and D's, i.e. atom P bonds to Q, as does T to U, while R separates from S.

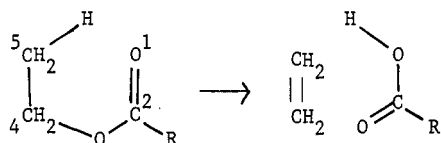
Example 1.10.6.1



ADAcy(C<1>,C<2>,3/C<2>,H,H,2/C<1>) [p2s + p2s + s2s]

**RULE 1.10.7** DADcy(P,Q,R,S,T,U) [n] - Represents reactions which are the reverse of the above.

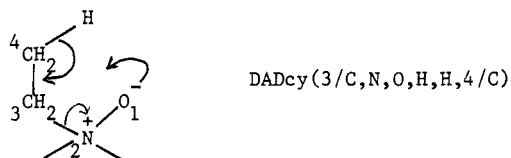
Example 1.10.7.1



DADcy(4/C,3/O,0,H,H,5/C) [6]

Here the stereoelectronic description has been conventionally shortened to [6] without specifying individual orbital types.

Example 1.10.7.2 - the Cope elimination, considered as an electrocyclic process



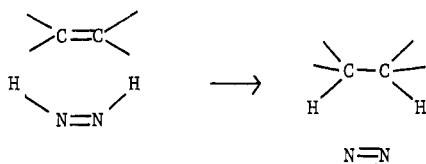
DADcy(3/C,N,O,H,H,4/C)

but if considered as an ionic process

A(O,H) D(4/C,H) Ap(4/C,3/C) D(N,3/C)

**RULE 1.10.8** - The above rules for electrocyclic processes can obviously be extended to more elaborate systems, with an A to represent each  $\sigma$ -bond formation, and a D to represent a breakage. An A should be written first if there are more associations than dissociations, a D if the reverse. If there are both types the second symbol should be different from the first. Subsequent symbols follow in the electrocyclic sequence defined implicitly by these rules.

Example 1.10.8.1 - simultaneous electrocyclic hydrogen transfer from di-imine to an olefin:



ADDAcy(C,H,H,N,2/N,H,H,2/C) [6]

Example 1.10.8.2 - the reaction of 1.7.3.1, using an electrocyclic mechanism:

ADAcy(C,H,H,B,B,2/C)

### Rule 1.11 conformational changes

Conformation changes can provide energy barriers, and so may be primitive changes which on their own form elementary reactions, or they may be part of elementary reactions which also involve other primitive changes. Designations can start with the symbol R (= Rotation).

**RULE 1.11.1** Ra(A) - Conformational shift of a molecule so that A is in an axial position in a ring.

**RULE 1.11.2** Re(A) - Conformational shift so that A is in an equatorial position in a ring.

**RULE 1.11.3** R(A,B) [n] (n = 0, 60, 120, 180 etc.) - Rotation about a bond so that the atoms A, B, attached to adjacent linked atoms, are at a dihedral angle of n.

## SECTION 2. REPRESENTATIONS OF ELEMENTARY REACTIONS

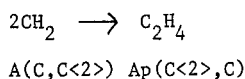
## Rule 2.1 the combination of primitive changes

Primitive changes represented as in Section 1 above can be combined, if they are concerted, by writing them successively on the same line. No punctuation is needed between the primitive change representations, but spaces are allowed to assist reading. The format of the primitive change representation above is chosen so that there is no confusion between the representations of successively written primitive changes, even though no punctuation intervenes. However if it is considered that a distinction should be made between "coupled" and "uncoupled"<sup>4</sup> primitive changes, even though the ER includes no intermediate of longer life than a molecular vibration (ca.  $10^{-13}$  s.), the uncoupled portions can be separated by a point ".". A sequence of P.C. representations represents an elementary reaction, and specifies how the reactants are transformed into the products.

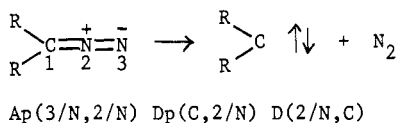
RULE 2.1.1 - A sequence needs to be defined for the order of writing of the concerted changes. If electronic charge is moving in a mechanism this charge should proceed from left to right as written, i.e. a nucleophilic addition will start with the attack of the nucleophile and finish with subsequent changes elsewhere in the molecule, while in an electrophilic addition the primitive change for the bonding of the electrophile will be at the right-hand end of the representation. If the sequence only involves shift of spin in an uncharged system the spin shall also move from left to right as written. It is convenient, but of no fundamental importance, for the equation to be written in the same way, i.e. arrows indicating electron shift should appear to point to the right on the paper wherever possible.

RULE 2.1.2 - When two bonds are formed or broken between the same atoms the  $\sigma$  formation should be written first, or the  $\sigma$  dissociation last.

Example 2.1.2.1

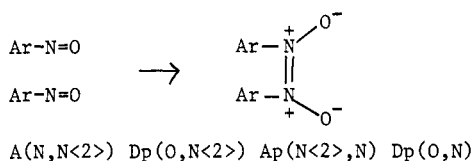


Example 2.1.2.2

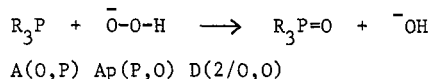


Example 2.1.2.3

dimerisation of nitrosobenzene



Example 2.1.2.4 - oxidation of a phosphine



A similar representation could be used where a ligand-metal bond is formed which involves both  $\sigma$  donation and  $\pi$  back donation.

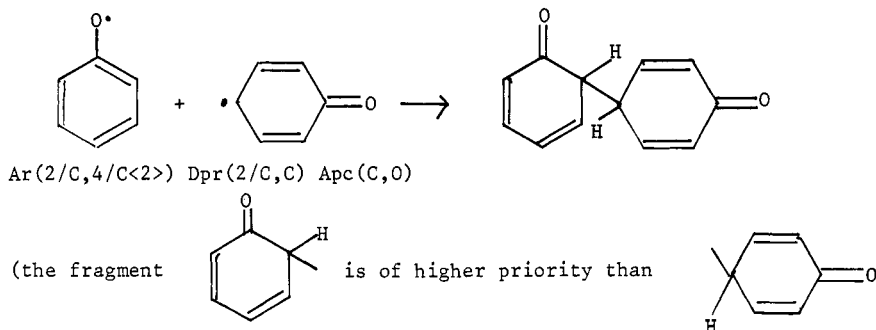
See also example 2.7.2

RULE 2.1.3 - When both "r" (radical) and "c" (colligation) terms occur in the same ER, "r" terms are written first if the reactant is a free radical, last if the product is.  
See example 2.1.5.1 below.

RULE 2.1.4 - Where two radicals interact the above rule does not define the order in which the P.C.'s are written. If one end of the sequence involves a  $\sigma$  bond formation it should be written first (example 1.4.3.1 above), lower priority being accorded to  $\pi$  bond formation,  $\sigma$  bond fission and  $\pi$  fission in that order.

**RULE 2.1.5** - If rule 2.1.4 does not provide an answer, and the system is not inherently symmetrical, there should be a primitive change which links two different fragments. The Cahn-Ingold-Prelog<sup>2</sup> priority rules should be applied to each fragment; the changes involving the lower priority fragment should be written first, and subsequent changes written in the direction of spin movement (2.1.1 above).

Example 2.1.5.



### Rule 2.2 the sequence of elementary reactions

The mechanism is written as a sequence of ER's which are normally assumed to proceed from left to right, or downwards as read. They are separated by a "+" sign. If a true intermediate is involved which however does not have time to undergo diffusional equilibration with the bulk solution, the ER's which form and destroy it are linked with a "\*" (asterisk) rather than "+". Examples 1.9.2.3 and 1.9.2.4 describe reactions which may be more accurately designated with a "\*" than a "+". See also example 1.9.2.1.

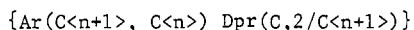
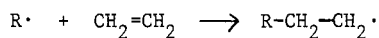
### Rule 2.3 rate limiting steps

The rate limiting elementary reaction may where relevant be optionally marked by the traditional transition state symbol "+", which is suffixed to the representation of the reaction: thus PC(P,Q):†. In the absence of a suitable symbol in machine-readable representations the "#" ("hash", "number", "square" or "sharp") symbol should be substituted for "+" and placed in line (i.e. not as a superscript). See examples 3.1.4.2, 3.1.4.3, 3.4.3.1 etc.

### Rule 2.4 chain reactions

A group of elementary reactions which form the propagation steps of a chain reaction are enclosed in distinctive braces, i.e. { }, to indicate that the sequence can be repeated. The molecule references <n>, <n+1> etc. can be used to indicate successive identical participant molecules (e.g. monomers).

Example 2.4.1 - olefin polymerisation by the radical mechanism

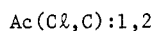
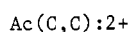
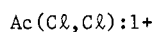
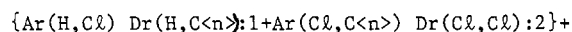
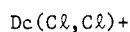
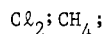


See also the  $S_{RN}1$  representation in the Table and examples 2.5.1 and 4.1

### Rule 2.5 competitive reactions

Reaction sequences which include alternative reaction paths can be indicated by appending to the appropriate alternative elementary processes a serial number. Elementary reactions which are in competition with each other are given the same serial number.

Example 2.5.1 - halogenation of hydrocarbon



chain terminating processes competitive with each step of the chain as indicated.

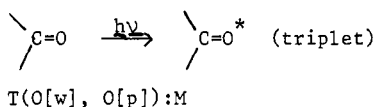
**Rule 2.6 general use of suffixes**

Other indicators (e.g. of stereochemistry) may be included after the relevant elementary process. These and the above indicators shall be known as the "suffix". They apply to the elementary reaction as a whole, not to individual PC's within it. They are separated from the string of PC's by a colon ":". If there are several suffixes they may be separated by commas.

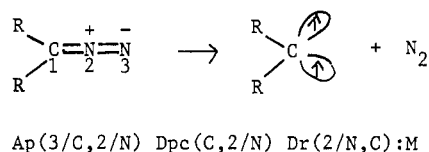
**Rule 2.7 spin changes**

Reactions which are accompanied by a change of spin multiplicity may be suffixed by the symbol M. Such changes would normally occur in colligations (rules 1.2.3, 1.3.3) and their reverse (1.4.3, 1.5.3) but singlet triplet conversions are also associated with electron transfers (rule 1.8.1) and even with heterolytic dissociations. The presence of a "c" in a PC representation (e.g. "Dc") thus implies a possible multiplicity change which may need to be specified if the fragments or reactants are spin-correlated.

Example 2.7.1

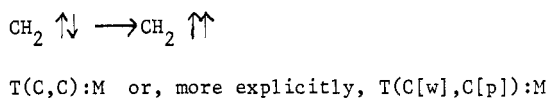


Example 2.7.2

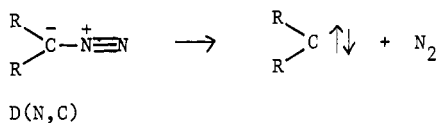


cf. Example 2.1.2.2 which is the spin paired dissociation. If there were no multiplicity change (M) the product would be in an excited singlet state.

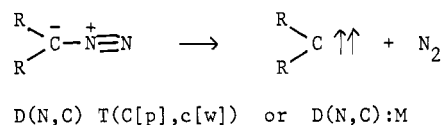
Example 2.7.3



Example 2.7.4



Example 2.7.5

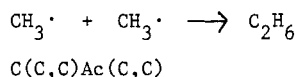


Note. 2.7.2 and 2.7.5 are of course the same reaction, but the difference in the notation reflects the different canonical form used as a starting point (see rule 3.1). See also examples 2.1.2.2 and 4.5.

**Rule 2.8 diffusion controlled reactions**

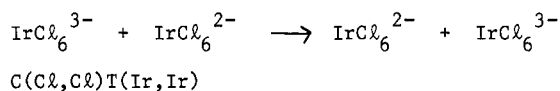
If in any ER the rate is determined primarily by a diffusion process in the bulk solvent rather than by the activation energy of itself or of any other ER, the representation may include an appropriate C or P term (see rule 1.9).

Example 2.8.1



Here the two  $\text{CH}_3\cdot$  fragments could for example be generated from two different molecules of  $\text{CH}_3-\text{N}=\text{N}-\text{CH}_3$ .

Example 2.8.2



### SECTION 3. REPRESENTATIONS OF STRUCTURES

In the rules above the generalised symbols P, Q etc. were used for atoms. This may be sufficient if only iso-electronic shifts are to be considered, but of course the mechanisms do depend both on the chemical natures of the atoms concerned and of their neighbours. Atom descriptors must therefore be defined, as must be the chemical natures of the reagents.

#### Rule 3.1 the minimal structure

A mechanistic model should be applied only to the minimum structure in which it is meaningful. All groups and atoms not involved in the model should be discarded. The test of "involvement" is whether at any stage in the mechanism there is a significant change in the bonding of the atom or group.

RULE 3.1.1 - The minimal structure can be obtained by replacing all non-involved atoms or groups by a hypothetical inert univalent group G. This can be formally regarded as a H atom for the purpose of numbering the structure (i.e. it is not included in the C-chain or as a specific substituent). In any machine-readable representation the minimum structure(s) must be specified, though in text or speech they may be omitted where this does not give rise to ambiguity. In the case of delocalised systems a particular resonance structure should be specified (normally that lowest in energy) see examples 2.7.2 and 2.7.4.

Example 3.1.1.1 - the minimal structure for any  $S_N1$  or  $S_N2$  reaction of any alkyl halide is  $CG_3X$ .

Example 3.1.1.2 - the minimal structure for addition to any alkene is  $CG_2 = CG_2$ .

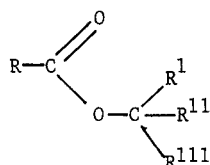
Example 3.1.1.3 - the minimal structure for E1, E2 etc. reactions is  $C_2G_5X$ .

RULE 3.1.2 - The atoms in a specific substrate as would be used in discussion of a specific example of a mechanism, are designated by the normal IUPAC positional numbers.<sup>7</sup>

RULE 3.1.3 - The atoms in a generalised substrate (i.e. the minimal structure) are designated using the same conventions as are recommended in the "Nomenclature in Organic Chemical Transformations",<sup>8</sup> i.e. relative positional numbers are written as post-slashed Arabic numerals such as "3/0" or "2/C", to indicate the oxygen atom at position 3 or the carbon atom at position 2, respectively.

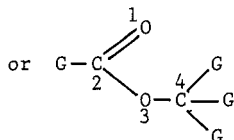
RULE 3.1.4 - When a chain of atoms in a minimal structure has to be numbered, the end with the higher atomic number, or if the same atom is at both ends, with the higher degree of unsaturation, is designated "1/". Heteroatoms are not omitted from the numbering, even at the end of a chain.

Example 3.1.4.1



as a substrate in ester hydrolysis

can be regarded as  $G-O-CG_3$  for the alkyl-oxygen fission routes (but see also example 3.4.4.2)

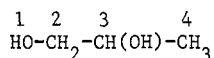


for acyl-oxygen fission routes; the carbonyl oxygen is then 0 and the other one 3/0

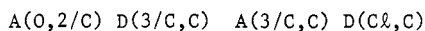
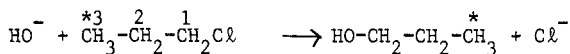




## Example 3.1.7.1 - pinacol rearrangement

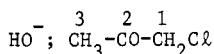


## Example 3.1.7.2 - hydroxy dehalogenation rearrangement

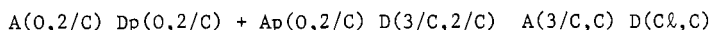


**RULE 3.1.8** - The locants assigned to atoms in the reagents are continued throughout the series of ER's which define a mechanism; atoms are not renumbered at each step.

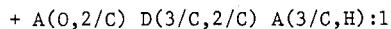
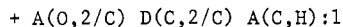
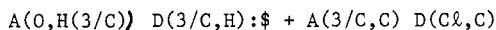
## Example 3.1.8.1 - Favorskii rearrangement



"Benzylic type" route:-



Cyclopropanone route:-

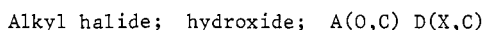
**Rule 3.2 indexing structures**

The minimal structures of the reagents must be specified in order to make clear what is the framework which is being modified by the reactions specified. A formula may be written out or described, but for indexing a suitable generic name might be used. The formulae or names should be written before the representation of ER's which operate on them, and can only be omitted when the reagents are clear from the context.

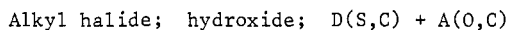
A formula index of minimal structures could be based on the sorting of the strings of atomic symbols of the chains, in the order defined by the numbering specified in rule 3.1.4, with minimal substituents essential to the mechanism appended.

Example 3.2.1 - the minimal structure of example 3.1.7.1 would be indexed as OCCO 0(3/C).

Example 3.2.2 - the "S<sub>N</sub>2" reaction of an alkyl halide with OH<sup>-</sup> should be represented



and the S<sub>N</sub>1 reaction



(see also any other examples in this report).

**Rule 3.3 reagent identification**

When it is not clear which atom belongs to which reagent a numeral should be applied to each reagent and used in the representation, enclosed in < >. The minimal structures given should be quoted with appropriate numerals, or assumed to be written in serial order. The symbol <1> can be omitted as redundant. The sequence in which the reagents are written down is normally the same as that in which each first appears in the representation of the reaction.

## Example 3.3.1 - the Diels-Alder reaction

ethene &lt;1&gt;; butadiene &lt;2&gt;;

followed by the mechanism as given in example 1.10.1.1 which could be expanded

AAcy(C,C&lt;2&gt;,4/C&lt;2&gt;,2/C) [p4s + p2s]

## Example 3.3.2 - Cannizzaro reaction

HO<sup>-</sup>, HCHO, HCHO, H<sup>+</sup>

A(O,C&lt;2&gt;) Dp(O,C&lt;2&gt;)

+ Ap(O,C&lt;2&gt;) D(H,C&lt;2&gt;) A(H,C&lt;3&gt;) Dp(O,C&lt;3&gt;) + A(O&lt;3&gt;,H&lt;4&gt;)

**Rule 3.4 special treatment of electrons, protons and delocalised systems**

A few situations exist where it is either not accurate or not helpful to use the specific chemical element notations as above for a particular reagent.

RULE 3.4.1 - The site of an electron may be represented by the symbols es (solvated) or eg (gas phase) or ec (conductor or semiconductor) where appropriate.

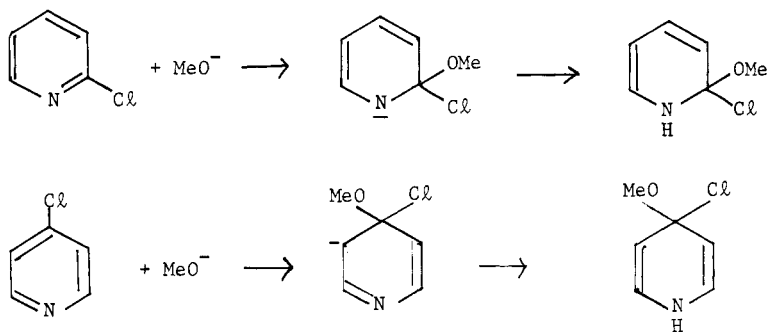
RULE 3.4.2 - In an electron transfer where the source or destination of an electron is unimportant or where a number of different species are involved and it is undesirable to specify a particular one, the symbol "Q" can be used. This can be regarded as a "wild card" or "joker" - a symbol for which the user may substitute any more specific symbol of his own choice.

Example 3.4.2.1 - transfer of an electron to the aromatic halide ArX in the S<sub>RN</sub>1 process from a variety of electron sources.

T(Q,X)

RULE 3.4.3 - The symbol \$ should be suffixed to a ER when details of bond rearrangement in conjugated systems do not need to be specified (see example 1.5.1.3), or where a particular rearrangement has been specified only because it is essential to the outcome of the ER (example 3.4.4.1 below).

Example 3.4.3.1 - the following two reactions are similar, giving products of which only one canonical form is indicated.



and can be written (first step)

A(O,2/C) Dp(2/C,N):\$ and A(O,4/C) Dp(4/C,3/C):\$

The subsequent protonation steps are

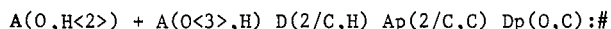
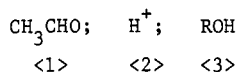
A(N,H) and Ap(3/C,2/C) Dp(2/C,N) A(N,H), respectively

The double bond shifts need only be written out in the second case where the reaction outcome necessitates it; they could however have been included in either (but not both) EP's of the reaction of 4-chloropyridine. See also example 1.9.2.2 for the use of "\$" with weak associations.

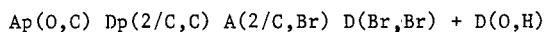


**RULE 3.4.5** - For rapid hydron transfer steps that are at equilibrium the acid (base) that donates (receives) the hydrogen is not specified, when it is not the reactant under consideration. This corresponds to specific acid (base) catalysis.

Example 3.4.5.1 - acid catalysed enolisation of a carbonyl compound



Bromination of the enol



See also examples 3.4.3.2, 3.1.4.4

## SECTION 4. FURTHER EXAMPLES OF THE APPLICATIONS OF THE RULES (see also Table, Section 6)

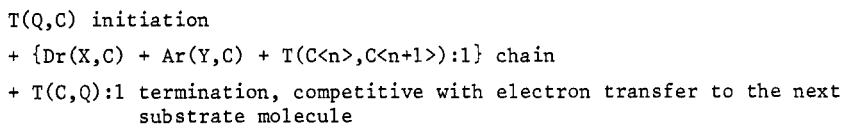
Section 6 includes all the reactions included in the parallel proposals of a System for the Symbolization of Simple Reaction Mechanisms,<sup>3</sup> with the addition of two extra processes [ $S_{\text{HAr}}$ ,  $S_{\text{Nlcb}}$  (carbene)]. The Symbolization and the detailed linear representation herein correspond quite closely in most cases. In order to derive the symbolization the "p" terms in the full name are ignored, and the subscript N is applied for (X,C) terms or E for (C,X) terms, terms not involving C not being given subscripts. Minor differences in order only appear in 1.5, 1.8 and 3.3. Although the objectives of the representation are different from those of the symbolization, compatibility has been maintained whenever possible.

### Example 4.1

A group of electron-transfer catalysis mechanisms have been referred to as  $S_{\text{RN}}^1$ ,  $S_{\text{RE}}^2$ ,  $S_{\text{ON}}^2$ ,  $S_{\text{OE}}^1$  where the substrate is reduced (R) or oxidised (O) and the radical form produced is subjected to a nucleophilic or electrophilic substitution. The product is then re-oxidised (or reduced) as appropriate, either regenerating the original catalyst or promoting a further substitution by exchange of the electron with a further substrate molecule. The steps of the  $S_{\text{RN}}^1$  reaction are thus (if Y replaces X)



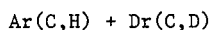
or if one wishes to indicate the subsequent chain nature of the process it can be written



In the related mechanisms given below (4.2 - 4.4) only the substitution step is notated; a full representation can be constructed as in this case.

### Example 4.2

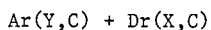
The  $S_{\text{RE}}^2$  process involves electrophilic addition to a radical, e.g.  $\text{H}^+$  might displace  $\text{D}^+$  in an anion radical



**Note.** This is an example of a "r" term in which the first atom descriptor is that of the radical, since the other atom involved is electron deficient (rule 1.2.2).

**Example 4.3**

The  $S_{ON}2$  process involves the preliminary oxidation step T(C,Q) followed by association with a nucleophile (Y) followed by loss of X

**Example 4.4**

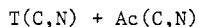
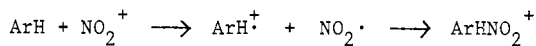
The  $S_{OE}1$  process involves dissociative exchange of an electrophile, e.g. loss of a proton from the  $\alpha$ -C of an amine radical cation



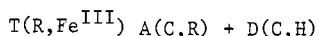
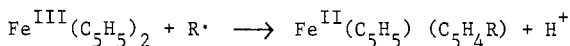
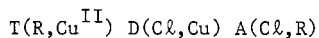
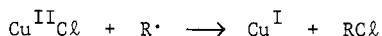
Note. The ordering of the atom descriptors specified in 1.2.2 is such that the electrophilic or nucleophilic partner occupies the same position as it would have in a D or A PC. The Ar or Dr (etc.) representations apply whether or not the odd electron participates directly in the bonding changes represented.

**Example 4.5**

A further example which mixes ionic and radical processes is one proposed mechanism for aromatic substitution

**Example 4.6**

Processes which involve electron transfer to or from transition metal orbitals can be represented by a T PC together with other PC's.

**SECTION 5. LIST OF SYMBOLS AND ABBREVIATIONS**

PC	Primitive change	preamble
ER	Elementary reaction	preamble
P,Q,R,S	etc. (in parentheses, separated by commas). Generalised symbols for atoms operated on by PC	rule 1.1
Q	A generalised symbol for an atom or group, which can be used where there are several alternatives	rule 3.4.2
G	Group. Used to indicate noninvolved substituents on a minimal structure	rule 3.1.1
2/	Relative position indicator of following atom (here position 2)	rule 3.1.3
<2>	Serial number of reagent containing atom immediately preceding e.g. 3/C<2> means the third C in reagent 2	rule 3.3
P(R)	Atom P which is a substituent on atom R, e.g. H(3/0) the hydrogen on O at position 3	rule 3.1.5, 3.1.6
A	Association	rule 1.2.1
Ar	Association, radical	rule 1.2.2
Ac	Association, colligative	rule 1.2.3
D	Dissociation	rule 1.3.1
Dr	Dissociation, radical	rule 1.3.2
Dc	Dissociation, to two radicals	rule 1.3.3
p	(as in Ap) Indicates pi-bond involved	rule 1.4, 1.5
U	Union, to form 3- or multi-centre species	rule 1.6.1

List of Symbols and Abbreviations (contd.)

V	Reverse of U	rule 1.6.2
I	Insertion of a single atom into a bond	rule 1.7.1
Ia	Insertion of two adjacent atoms	rule 1.7.3
X	Extrusion (reverse of I)	rule 1.7.2
T	Transfer of a single electron	rule 1.8
C	Diffusional combination (weak association)	rule 1.9
P	Parting (reverse of C)	rule 1.9
R	Rotational (conformational) steps	rule 1.11
cy	(as in ADAcy) Electrocyclic process	rule 1.10
es, eg, ec	A "free" electron with an indication of its site	rule 3.4.1
[ ]	Enclose orbital or electron information (see also example 1.8.1.4, 2.7.3)	rule 1.10.1
w, s, p, a, s	They may also enclose conformational information (within [ ]) Conventional electronic designations transliterated into the English alphabet when necessary	rule 1.11.3
+	Coupling between consecutive ER's	rule 2.2
*	As +, but where the intermediate does not equilibrate with bulk solution	rule 2.2
. (point)	Used for linking "uncoupled" PC's into an ER	rule 2.1
space	Can be used, or omitted, between PC's in an ER or elsewhere as desired, other than within a PC designation. (It is recommended that PC representations should be separated by spaces for legibility, but that spaces should not be used to divide up the parameters within the PC parenthesis. On no account must a PC designation, or a conventional chemical atomic symbol, be split by a space. Spaces are also used conventionally within "[ ]". As spaces have no significance as terminators they can be stripped before storage of representation strings in a computer, as in the typical representations given in the Table)	
:	Used to separate a suffix from the rest of a ER	rule 2.6
#	Suffix indicating rate-limiting step	rule 2.3
2	(as suffix) Serial number of ER	rule 2.5
{ }	Repeat the ER's within the braces	rule 2.4
M	Suffix indicating a spin multiplicity change	rule 2.7
\$	Suffix to indicate a delocalised system	rule 3.4.3
;	Used as separator in list of reagent species	rule 3.2
, (comma)	Used as separator between atom representations in PC or between suffixes where there is more than one suffix	example 2.5.1
(new line)	Can be used between ER's or PC's as required, but splitting the representation of an ER between two lines is not recommended. New line is not synonymous with "+". Nevertheless in a table it may be convenient to split an ER between two lines (see Table for more examples)	example 3.1.8.1 example 2.5.1
/	Relative positional indicator	rule 3.1.3
< >	Brackets to enclose the serial number of a reagent molecule	rule 3.3
( )	Brackets to enclose details of the atoms acted on by a PC (i.e. the PC parameter list)	rule 1
	Also brackets within a PC parameter list which enclose supplementary positional information	rules 3.1.5, 3.1.6
C, N, Br etc.	Standard atomic symbols	
C.I.P	Cahn-Ingold-Prelog priority rules (ref. 5)	
n	A generalised integer, as in "the nth molecule".	

Note. The symbols used in the representation are deliberately restricted to the printable ASCII character set, without superscripts, subscripts, alternative type faces, etc. Any modifications or extensions to these symbols should be chosen from the same character set.

## SECTION 6. TABLE

Comparison of all names proposed in the 'System for Symbolic Representation of reaction mechanisms' (ref. 3) with corresponding Ingold-type names and with the linear representation proposed in this document

Example Number in ref. 3	Ingold-type Name	Proposed Representation	Proposed Symbolization
<u>SUBSTITUTION MECHANISMS</u>			
1.1a	$S_N2$	$A(X,C)D(Y,C)$	$A_N D_N$
1.1b	$S_N2'$	$A(X,C)Dp(2/C,C)Ap(2/C,3/C)$ $D(Y,3/C)$	$3/1/A_N D_N$
1.2a	$S_E2$	$D(C,X)A(C,Y)$	$D_E A_E$
1.2b	$S_E2'$	$D(C,Y)Ap(C,2/C)Dp(3/C,2/C)$ $A(3/C,X)$	$1/3/D_E A_E$
1.3	$S_N2cA$ or $A2$	$A(Y,Z)+A(X,C)D(Y,C)$	$A_e + A_N D_N$
1.4	none	$A(Z,X)+D(C,X)A(C,Y)$	$A_n + D_E A_E$
1.5	$S_EC$ or $S_E2$ coord	$A(Z,X)+D(C,X)A(C,Y)D(Z,Y)$	$A_n + A_E D D_E$
1.6a	$S_Ei$ or $S_F2$	$A(Z,X)D(C,X)A(C,Y)D(Z,Y)$	$A_E D A D_E$
1.6b	$S_Ei'$	$A(Z,X)D(C,X)Ap(C,2/C)$ $Dp(3/C,2/C)A(3/C,Y)D(Z,Y)$	$3/1/A_E D A D_E$
1.7	$S_NAr$ or $Ad_N-E$ or $B_{AC}2$	$A(X,C)Dp(2/C,C)+Ap(2/C,C)D(Y,C)$	$A_N + D_N$
1.8a	none	$A(Y,C)Dp(2/C,C)+A(Z,E)+$ $Ap(2/C,C)D(Z,C)$	$A_N + A_e + D_N$
1.8b	$A_{AC}2$	$A(O,H)+A(X,C)Dp(2/C,C)+A(Z,E)+$ $Ap(2/C,C)D(Z,C)+D(O,H)$	$A_h + A_N + D_h A_h +$ $D_N + D_h$
1.9	$S_E2Ar$	$Dp(C,2/C)A(C,X)+D(C,Y)Ap(C,2/C)$	$A_E + D_E$
1.10a	$S_N1$ or $B_{AL}1$	$D(Y,C)+A(X,C)$	$D_N + A_N$
1.10b	$S_N1'$	$Dp(2/C,C)Ap(2/C,3/C)D(Y,3/C):\$$ $+A(X,3/C)$	$1/D_N + 3/A_N$
1.11	$S_E1$	$D(C,Y)+A(C,X)$	$D_E + A_E$
1.12	$S_N1cA$ or $A1$	$A(Y,Z)+D(Y,C)+A(X,C)$	$A_e + D_N + A_N$
1.13	none	$A(Z,Y)+D(C,Y)+A(C,X)$	$A_n + D_E + A_E$
1.14	$S_E1(N)$ or $S_E1-X^-$	$A(Z,Y)D(C,Y)+A(C,X)$	$A_n D_E + A_E$
1.15	none	$D(Y,C)+D(X,Y)+A(X,C)$	$D_N + D + A_N$
<u>ADDITION MECHANISMS</u>			
2.1	$Ad3$	$A(X,C)Dp(2/C,C)A(2/C,Y)$	$A_N A_E$
2.2	none	$Ia(X,C,2/C,Y)$	$A_N D A_E$
2.3	none	$AAcy(X,C,2/C,Y)$	cyclo-AA
2.4	none	$A(X,C)Dp(2/C,C)+A(2/C,Y)$	$A_N + A_E$
2.5	none	$Ap(C,2/C)A(C,Y)+A(X,2/C)$	$A_E + A_N$

/Table contd....



TABLE (Contd.)

Example Number in ref. 3	Ingold-type Name	Proposed Representation	Proposed Symbolization
<u>ELIMINATION MECHANISMS</u>			
3.1	none	$D(C,Y)Ap(C,2/C)D(X,2/C)$	$D_E D_N$
3.2	E2 or E2H	$A(X,Y)D(C,Y)Ap(C,2/C)D(Y,2/C)$	$AD_E D_N$
3.3	$E_i$	$A(X,Y)D(C,Y)Ap(C,2/C)D(X,2/C)$	$D_N AD_E$
3.4a	$E_2cA?$	$A(X,E)+D(C,Y)Ap(C,2/C)D(X,2/C)$	$A_e + D_E D_N$
3.4b		$A(X,E)+A(Z,Y)D(C,Y)Ap(C,2/C)D(X,2/C)$	$A_e + A_n D_E D_N$
3.5	E1	$D(X,C)+D(C,Y)Ap(C,2/C)$	$D_N + D_E$
3.6	E1	$D(Y,C)+A(Z,Y)D(C,Y)Ap(C,2/C)$	$D_N + A_n D_E$
3.7	ElcA	$A(X,E)+D(X,C)+A(Z,Y)D(2/C,Y)Ap(2/C,C)$	$A_e + D_N + A_n D_E$
3.8	ElcB	$A(Z,Y)D(C,Y)+Ap(C,2/C)D(X,2/C)$	$A_n D_E + D_N$
Carbene formation	$S_N1cb$	$D(C,X)+D(Y,C)$	$D_E + D_N$
<u>HOMOLYTIC MECHANISMS</u>			
4.1	$S_H^2$	$Ar(Y,X)Dr(Y,C)+Ar(Z,C)Dr(Z,X)$	$AD_R + A_R D$
4.2	$S_H^1$	$Dc(C,Y)+Ar(Z,C)Dr(Z,X)$	$D_R + A_R D$
4.3	$S_{RN}^1$	$\{T(D,Y)+Dr(Y,Ar)+Ar(X,Ar)\}$	$T + D_N + A_N$
4.4	none	$Ar(C,X)Dpr(C,2/C)+Ar(Y,C)Dr(Y,X)$	$A_R + A_R D$
Homolytic aromatic substitution of Y by X	$S_HAr$	$Ar(C,X)Dpr(C,2/C)+Apr(C,2/C)Dr(C,Y)$	$A_R + D_R$

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