A NEW SYSTEM OF MOLECULAR REARRANGEMENTS

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The present classification introduces — beside the generally accepted 1,2-rearrangements — the main group of 1,3-rearrangements including several of the well-known rearrangements (allyl-, CLAISEN-, FRIES-, WÖHLER-, SOMMELET-, FISCHER-HEPP-, ORTON-, HOFFMAN-MARTIUS- *etc.* rearrangements). At the same time the tautomer-changes have also been classified here. The author also gives the classification by subgroups of the more important rearrangement reactions, taking into consideration their generally accepted mechanism in literature.

According to the basic classification of reactions in organic chemistry, besides substitution-, addition- and elimination-processes, the fourth group is given by molecular rearrangements. The systematization of the latter have been undertaken starting from the most diverse points of view [1—7]. In order to throw light to newer processes and their mechanisms we are in need of such a systematization, such a „form", which is in accordance with the theory of evolution. "Any phenomena of nature and society comes from a certain concrete material *content* and of a corresponding *form.*" As the dialectical interaction of substance and form indicates, the latter always actively affects the former, promotes or hinders its development. New arrangements are generally made necessary by this law of marxist philosophy. By times the collecting of a great number of experimental data, their explanation helped to form such a system, within the frames of which the content — study of the processes and their mechanisms — could develop wit a marked speed. The old system proved too be to tight for further investigations, it was hindering knowledge, a new form became necessary. The conclusions given in the introduction of our earlier paper as well as its experimental results support this statement [8].

By *molecular rearrangement* we understand all the processes, where, as a result of chemical changes, the newly entering ion or radical does not take an identical place with the losing ion or radical. Molecular rearrangements otherwise are called isomerisation reactions. However, in this respect literature does not reflect a uniform standpoint. During *isomerisation* the structure of molecule also changes without the elementary constitution of the molecule being changed. We are of the opinion that the two definitions mean essentially changes of the same structure. The misunderstanding comes so that processes treated by literature as molecular rearrangements are compound in general. However, the essence of the whole change is given by an isomerisation step and we dot not consider it reasonable to treat separately, under different designations rearrangements, being theoretically of similar character.

In the present work we have started from the generally accepted Wheland classification [1] with the only difference that the main group of 1,3-rearrangements is introduced and furthermore, in accordance with some other classifications, even the tautomer changes are regarded as belonging here. We think it superfluous to give an indication of this. The basic idea was given by problems occurring in the study of chemical changes of 1,3 bifunctional compounds. The resolving of these problems likely will lead to the widening of the circle of 1,3-rearrangements.

In essence the classification can be described as follows. The main groups are given by 1,2-, 1,3- and 1,*n*-rearrangements. Within these, according to the mechanism of the processes, there are nucleophyl (N)-, electrophyl (E)-, radical (R)-type, intra (Ia)- or intermolecular (Ir)-rearrangements. Introducing designation letter I (isomerisation), the subgroups can be signed in the following manner:

Table I

1,2	1,3	1,n
rearrangement		
$1,2\ I_{NIa}$	$1,3\ I_{NIa}$	$1,n\ I_{NIa}$
$1,2\ I_{NIr}$	$1,3\ I_{NIr}$	$1,n\ I_{NIr}$
$1,2\ I_{EIa}$	$1,3\ I_{EIa}$	$1,n\ I_{EIa}$
$1,2\ I_{EIr}$	$1,3\ I_{EIr}$	$1,n\ I_{EIr}$
$1,2\ I_{RIa}$	$1,3\ I_{RIa}$	$1,n\ I_{RIa}$
$1,2\ I_{RIr}$	$1,3\ I_{RIr}$	$1,n\ I_{RIr}$

No systematization can be regarded as a closed, steady one, since it is always ubjected to chasnges with the progress of knowledge. Within the main groups there may occur transitional groups, too. *E. g.* most of the examples of the Fries-rearrangement can be classified into the group $1,3\ I_{EIa}$. At the same time there are cases when the acyl cation migrates into a para-position and the mechanism may be intermolecular.

Today it is yet impossible to give an exact classification of all the known rearrangement reactions. This predisposes first of all a through knowledge of the mechanism of the processes and there are complications about this. As to the mechanism of some subgroups of 1,2-rearrangements a general view can be traced in literature. However, the mechanism of 1,3- and 1,*n*-rearrangements, resp., is much more complicated than it can be seen in Table I, since the chain-like 1,2-migrations may occur with less change in the energy as compared to the direct 1,3- and 1,n-migrations, resp.

Radical-type isomerisation changes have been dealt with only in the course of the last years. Among them a great number of 1,3-rearrangements are to be found [as *e. g.* 3, 6, 9]. Their mechanism being uncleared so far, we disregard to classify them at the present time. Rearrangements on contact catalysts, especially taking place at relatively low temperatures on surfaces with more or less electrons are not rearrangements of the radical type, but they can be treated in a way similar to that of nucleophyl or electrophyl rearrangements.

In this respect first of all we note that a corresponding alteration of the conditions can easily turn a heterolytic isomerisation change into a homolytic one. what considerably enlarges the circle of radical type rearrangemets.

In the following we are giving the classification of the more important rearrangement reactions according to the view-points outlined above, taking into consideration their generally accepted mechanism.

$1,2\ I_{NIa}$: Pinacolin, Wagner—Meerwein-, Demianov-, Tiffeneau-, Beckmann-Danilov-, Nametkin-, benzyl-type-rearrangements, Curtius-, Schmidt-, LOSSEN- and HOFMANN decompositions, isomerisation of epoxides to oxo-compounds.

1,2 I_{EIa}: WITTIG-, STEVENS-, ARBUZOV-rearrangements.

1,3 I_{NIa}: Allyl-rearrangement and the rearrangement of 1,3-diols and their derivates to oxo-compound (mechanism yet unproved).

1,3 I_{NIr}: A less group of tautomer-rearrangements (anionotrop rearrangements).

1,3 I_{EIa}: CLAISEN-, FRIES- (the mechanism may be even intermolecular), SOMMELET-, WÖHLER- rearrangements, that of iminoanylines and amidines, N-arylsulfamin acids, nitroanylines (the mechanism may be intermolecular, too).

1,3 I_{EIr}: Most of tautomer rearrangements (prototrop rearrangements), certain types of the HOFMANN—MARTIUS-rearrangement, FISCHER—HEPP-, ORTON-rearrangements, the rearranngement of alkylanylines.

1,n I: This group includes the transannular rearrangements and that of the benzidine. Mention must be made of side reactions directed to para-situation occuring at the 1,3-rearrangements of some aromatic compounds. As the group of 1,n-rearrangements is increasing and the mechanisms are more and more thoroughly understood, in the future it seems possible to form more main groups.

The importance of this new classification may be sought in the following:

1. It gives a better arrangement of the numerous experimental data.
2. Promotes to solve the doubtful problems.
3. Gives rise to newer questions.

This new classification of molecular rearrangements is in its present form only a preliminary communication. The characteristics of the main- and sub-groups, their mechanisms, the collected data in literature and their discussion together with experimental results will be published later.

НОВАЯ СИСТЕМА МОЛЕКУЛЯРНЫХ ПЕРЕГРУППИРОВОК

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В новой систематизации автором была принята—кроме общепринятых 1,2-перегруппировок группа 1,3-перегруппировки, к которой принадлежат несколько из известных перегруппировок как напр. аллильное-перераспределение, перегруппировка *Клайзена. Фриза*, *Велера*, *Сомелета*, *Фишера-Геппа*, *Ортона*, *Гофтан-Марциуса* и т. д. В то же время таутомерные перегруппуровки были также приняты как 1,3-перегруппировки. В настоящей работе дается подгруппуровка важнейших реакций перегруппиовки — имея в виду их общеизвестный по лутературным данным механузм.

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