ELECTRONIC CONCEPTION IN ORGANIC CHEMISTRY. II. AN INTERPRETATION OF THE REARRANGEMENTS OF TRISUBSTITUTED α-GLYCOLS.*

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It has been brought to light that the trisubstituted α-glycols may be dehydrated by acids and undergo subsequent transposition in three ways: (I) by the *semihydrobenzoin rearrangement* it gives a trisubstituted aldehyde with the elimination of the tertiary OH-group; (II) by the *vinyl dehydration* the tertiary OH is removed, yielding a ketone without changing the skeletone of the carbon chain; and (III) by the *semipinacolin rearrangement* a ketone is formed with the removal of the secondary OH-group.

$$\mathrm{RR'C\,(\mathbf{OH})\cdot CHR''\,(O\,\mathbf{H}) \longrightarrow (RR'\underset{\bullet}{C}\cdot CHR''(O\cdot)) \longrightarrow RR'R''C\cdot CHO} \;\ldots(\mathrm{\ I\ })$$

$$\mathrm{RR'C\,(\mathbf{OH})\cdot CHR''\,(O\,H) \longrightarrow (RR'C{=}CR''(OH)) \longrightarrow RR'CH\cdot CO\cdot R''} \ldots(\mathrm{II})$$

$$\mathrm{RR'C\,(O\,\mathbf{H})\cdot CHR''\,(\mathbf{OH}) \longrightarrow (RR'C\,(\dot{O}\cdot)\cdot \underset{\bullet}{C}HR'') \longrightarrow R\cdot CO\cdot CHR'R''} \ldots(\mathrm{III})$$

The first occurs almost exclusively by the action of boiling dilute sulphuric acid, and the other two either by the same reagent or by cold concentrated sulphuric acid, the nature of the substituents also influencing the direction of the rearrangements. These transpositions have been studied from various points chiefly by French chemists, above all, Orékhoff, Tiffeneau and Lévy, but they have not gone the length of interpreting these rearrangements from one and the same standpoint, for the rearrangement is so manifold as appears to be particular to each type of the glycols. It is attempted, in this paper, to throw a light on the mechanism of these rearrangements by applying the theory of alternate polarity and the relative electronegativity of organic radicals on the pile of experimental data given by the above mentioned and other chemists. According to Kharasch and his colaborators the electronegativity of some organic radicals are in the following order:

$$p\text{-}\mathrm{CH_3O\cdot C_6H_4}{-} > \alpha\text{-}\mathrm{C_{10}H_7}{-} > \text{Halogenophenyl} > \mathrm{C_6H_5}{-} > \mathrm{CH_3}{-} >$$
$$\mathrm{C_2H_5}{-} > \text{n-}\mathrm{C_3H_7}{-} > \text{n-}\mathrm{C_4H_9}{-} > \mathrm{C_6H_5\cdot CH_2}{-}^{**}$$

In order to explain the influence exerted by the acids a presumable assumption is made that *the dilute acid dehydrates catalytically*, as in case

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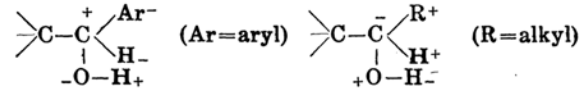
*In the previous paper, (this Bulletin, **3** (1928), 308–316), the rearrangements of pinacones and tertiary amino-alcohols are discussed.

of pinacones and tertiary amino-alcohols, whereas *the concentrated acid acts substitutionally*. In this way, (1) we can explain clearly complicated influences exercised by various substituents as well as dehydrating agents, and can look through the rearrangements of all the glycols in question from one point. (2) We can afford theoretical basis to many facts and laws which have been established experimentally, including the problems of the migratory tendency of organic radicals. Thus the interpretation based on the electronic theory of valence would appear to offer a good working hypothesis.

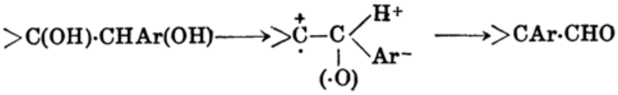
I. Rearrangements by Dilute Sulphuric Acid.

1. Glycols with negatively polarized tertiary OH-groups. Owing to the highly positive character of hydrogen, nearly all trisubstituted α-glycols have their tertiary hydroxyls negatively polarized. Therefore, if the dilute acid dehydrates catalytically according to the mechanism discussed in the previous paper, it must be the tertiary OH that attracts the H-ion of the acid, whereas we have two H-atoms which can combine with the anion of the acid, i.e. that of the secondary OH-group and that attached to the secondary carbon. This alternative will be influenced by the substituent in the secondary carbon in such a manner as to discriminate the polarity of the two H-atoms in question. The presence of a negative radical such as aryl, in the secondary carbon, produces a lessening effect on the negative polarity of this carbon, and this causes the adjoining hydrogen to be induced negative and that of hydroxyl positive, consequently it should be the latter hydrogen which will be brought with greater ease into ionic state (1a); on the other hand, the reverse holds in case of a glycol with an alkyl group in the secondary carbon (1b). Thus we have two different cases according to the negativity of the substituent in the secondary carbon.



(a) *Glycols with a grouping—CHAr(OH).* By the elimination of water it gives such a fraction of the molecule as RR′C·CHAr(O·), as can be seen from the reason just described, and subsequently one of the two substituents attached to the secondary carbon, either the hydrogen or the aryl, migrates to the tertiary carbon. But owing to the positive polarity of this carbon, it must be the aryl, the more negative group of the two, that wanders, giving a trisubstituted aldehyde (semihydrobenzoin rearrangement).

Kharasch and others, *J. Chem. Education*, **5 (1928), 408. This table contains some corrections and complements to the old one given in the previous paper.



$$>C(OH)\cdot CHAr(OH) \longrightarrow >\overset{+}{\underset{\cdot}{C}}-\underset{\underset{(\cdot O)}{|}}{C}\begin{matrix}\diagup H^{+}\\ \diagdown Ar^{-}\end{matrix} \longrightarrow >CAr\cdot CHO$$

Ex.* 1. $PhRC(OH)\cdot CHPh(OH)\rightarrow Ph_2RC\cdot CHO$, where R=Me**(6), Et,(6) Pr(13), iso-Bu(17), iso-Am.(17)

2. $R_2C(OH)\cdot CHPh(OH)\rightarrow PhR_2C\cdot CHO$, where R=Me(6), Et(18), Pr(18).

3. $R_2C(OH)\cdot CHAnis(OH)\rightarrow AnisR_2C\cdot CHO$, where R=Me(23), Et(18), Ph(14), Anis.(14)

4. $RR'C(OH)\cdot CHAnis(OH)\rightarrow Anis\ RR'C\cdot CHO$, where $\begin{matrix}R=\\ R'=\end{matrix}\begin{cases}Me^{(26)},\\ Et,\end{cases}\begin{cases}Anis^{(8)},\\ Bzl.\end{cases}\begin{cases}Anis.^{(9)}\\ Ph.\end{cases}$

In spite of the presence of the typical grouping —ArCH(OH), triaryl glycols $Ar_2C(OH)\cdot CHPh(OH)$, where $Ar_2=Ph_2$(5), (Ph, Anis)(14) and $Anis_2$(14), are not subject to semihydrobenzoin rearrangement but to vinyl dehydration, while the corresponding glycols with the grouping —CHAnis(OH), undergo semihydrobenzoin rearrangement, as is seen in the Ex. 3 and 4. These abnormal glycols have two characteristics in their structure; namely (i) both groups attached to the tertiary carbon are strongly negative, and (ii) the aryl radical bound to secondary carbon is phenyl and not anisyl. These characteristics account for the abnormal behaviour and prove that the state of polarity in these molecules is favourable to vinyl dehydration. Thus the accumulation of positivity on the part of the tertiary carbon due to the two aryl groups, will cause such a strongly negative polarity in the secondary carbon as being free from the influence exerted by the adjoining phenyl. Consequently the hydrogen bound to this carbon will be imparted with positive polarity; and this results in vinyl dehydration of the glycols in question. This unusual induced negativity on the part of the secondary carbon will be first reduced when the phenyl is replaced with anisyl, the most negative group, and semipinacolin rearrangement reappears. Thus it will be seen that these apparent contradictions make by no means an objection against the above electronic views, but on the contrary, afford a powerful support for them.

(b) *Glycols with grouping —CHR(OH).* These glycols, when dehydrated, should give derivatives of vinyl alcohol, $>C=C(OH)R$, as discussed above, which, being unstable, isomerize into their keto-form, $>CH\cdot CO\cdot R$, by the catalytic action of the acid present. This keto-enol isomerisation

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*Following symbols are adopted: Am=Amyl, Anis=*p*-Anisyl, Ar=Aryl, Bu=Butyl, Bzl=Benzyl, Et=Ethyl, Nap=Naphthyl, Ph=Phenyl, Pr=Propyl.

**For the convenience's sake, the literatures concerning to examples are collected in the end of this paper.

has already been interpreted as *prototropy* by Lowry* from the electronic standpoint.

$$\mathrm{R'_2C(OH)\cdot CHR(OH)\rightarrow R'_2C{=}C(OH)R\rightarrow R'_2CH\cdot CO\cdot R}$$

Ex. 5. $\mathrm{R'{=}Ph;\ \ R{=}Me^{(4)},\ \ Ph_2CH{-}^{(23)}}$.

$$6.\ \ \begin{array}{l}\mathrm{R'=}\\ \mathrm{R\ =}\end{array}\left\{\begin{array}{l}\mathrm{Me^{(1)}},\\ \mathrm{Me},\end{array}\right. \left\{\begin{array}{l}\mathrm{Me^{(7)}},\\ \mathrm{iso\text{-}Pr},\end{array}\right. \left\{\begin{array}{l}\mathrm{Me^{(20)}},\\ \mathrm{Bzl},\end{array}\right. \left\{\begin{array}{l}\mathrm{Me_{(23)}},\\ \mathrm{Ph_2CH{-}},\end{array}\right. \left\{\begin{array}{l}\mathrm{Et^{(3)}},\\ \mathrm{Me},\end{array}\right. \left\{\begin{array}{l}\mathrm{Et,^{(3)}}\\ \mathrm{Bzl},\end{array}\right. \left\{\begin{array}{l}\mathrm{Et^{(20)}},\\ \mathrm{Bzl},\end{array}\right. \left\{\begin{array}{l}\mathrm{Bzl^{(23)}}.\\ \mathrm{Me}.\end{array}\right.$$

2. Glycols with negatively polarized secondary OH-groups. Glycols of this type are very rare from the reason already mentioned; but if the tertiary carbon is combined to strongly electropositive radicals, and the secondary carbon to a highly negative group, it may be the case that the secondary hydroxyl is induced negative. Actually, glycols $\mathrm{Bzl_2C(OH)\cdot CHAr(OH)}$, where $\mathrm{Ar{=}Ph^{(18)}}$ or $\mathrm{Anis^{(24)}}$, are subject to neither semihydrobenzoin rearrangement nor vinyl dehydration, but to semipinacolin transformation as follows:

$$\mathrm{Bzl_2C(OH)^{+}\cdot CHAr(OH)^{-}\rightarrow Bzl_2C(O\cdot)\cdot\underset{\bullet}{C}HAr\rightarrow Bzl\cdot CO\cdot CHBzlAr.}$$

Summary. A delicate relation between the state of polarity in the molecule and the mode of dehydration by dilute sulphuric acid manifests itself in the rearrangements of the glycols $\mathrm{R_2C(OH)\cdot CHR'(OH)}$, which are tabulated as under. This table serves also as a summary to the present chapter.

Typical reactions of $\mathrm{R_2C(OH)\cdot CHR'(OH)}$ by dil. $\mathrm{H_2SO_4}$.

R′ R		− ← +			
		Anis	Ph	Me	Bzl
−	Anis	H	V		
↑	Ph	H+V	V	V	
	Me	H	H	V	V
+	Bzl	P	P	V	No Reaction

H=Semihydrobenzoin–, P=Semipinacolin-rearrangement, V=Vinyl dehydration.

II. Rearrangements by Concentrated Sulphuric Acid.

It is a probable assumption that the dehydration by concentrated sulphuric acid takes place substitutionally, since we can prove it experimentally

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*Cf. *J. Chem. Soc.*, **127** (1925), 1371.

in case of primary alcohols. In a dihydric alcohol we may have selective substitution of the two OH-groups; and in case of a trisubstituted α-glycol, different from the case of a pinacone, the polarity difference of the two hydroxyls is not the only factor to affect this selection, for secondary and tertiary hydroxyls are not same in the ease for substitution. Namely, the former is substituted with greater ease as is seen, for example, in the Schotten and Baumann's reaction. It seems that this sterical influence is so strong that it overcomes some negative polarity on the part of the tertiary hydroxyl, so long as this is not marked, resulting in elimination of the secondary hydroxyl. Therefore, it is the degree of polarity developed in the molecule, and not its mere sence, that plays an important rôle in the rearrangements by concentrated sulphuric acid.

1. Glycols with marked polarity. (a) *Glycols with negatively polarized tertiary OH-groups.* In these commonest case, sulphuric acid attacks the tertiary hydroxyl substitutionally, inducing the secondary carbon strongly negative. As this causes the increase of the positive character of the hydrogen bound to this carbon, vinyl dehydration should result.

$$>\mathrm{C(OH)\cdot CHR(OH)} \rightarrow \,>\mathrm{C(SO_4H)\cdot CHR(OH)} \rightarrow \,>\mathrm{C{=}C(OH)R} \rightarrow \,>\mathrm{CH\cdot CO\cdot R}$$

Ex. 7. $\mathrm{Ph_2C(OH)\cdot CHR(OH) \rightarrow Ph_2CH\cdot CO\cdot R}$, where R = Me(4), iso-Bu(17), Bzl(20), Ph(9).

8. $\mathrm{PhRC(OH)\cdot CHPh(OH) \rightarrow PhRCH\cdot CO\cdot Ph}$, where R = Me(12), iso-Bu(17), Ph(9), Nap(21).

9. $\mathrm{PhRC(OH)\cdot CHR(OH) \rightarrow PhRCH\cdot CO\cdot R}$, where R = Et(18), Pr(18).

10. $\mathrm{R_2C(OH)\cdot CHR'(OH) \rightarrow R_2CH\cdot CO\cdot R'}$, where,

$$\begin{matrix} \mathrm{R} = \\ \mathrm{R'} = \end{matrix} \left\{ \begin{matrix} \mathrm{Me}^{(1)}, \\ \mathrm{Me}, \end{matrix} \right. \left\{ \begin{matrix} \mathrm{Me}^{(7)}, \\ \text{iso-Pr}, \end{matrix} \right. \left\{ \begin{matrix} \mathrm{Me}^{(20)}, \\ \mathrm{Bzl}, \end{matrix} \right. \left\{ \begin{matrix} \mathrm{Me}^{(23)}, \\ \mathrm{Ph_2CH}\text{–}, \end{matrix} \right. \left\{ \begin{matrix} \mathrm{Et}^{(20)}, \\ \mathrm{Me}, \end{matrix} \right. \left\{ \begin{matrix} \mathrm{Et}^{(20)}, \\ \mathrm{Bzl}, \end{matrix} \right. \left\{ \begin{matrix} \mathrm{Bzl}^{(23)}. \\ \mathrm{Me}. \end{matrix} \right.$$

(b) *Glycols with negatively polarized secondary OH-groups.* It goes without saying that semipinacolin rearrangement takes place in these few cases.

Ex. 11. $\mathrm{Bzl_2C(OH)^{+}\cdot CHR(OH)^{-} \leftarrow Bzl_2C(O\cdot)\cdot CHR \rightarrow Bzl\cdot CO\cdot CHRBzl}$, where R = Ph(18), Anis(24).

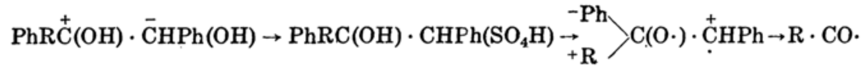
2. Glycols without marked polarity. These glycols are generally subject to semipinacolin rearrangement as the result of predominance of the sterical influence over the effect due to polarity. In this rearrangement one of the two groups combined to the tertiary carbon undergoes either simple or selective migration according to the type of the glycols in question.

(a) *Case of simple migration.* When the substituents in the tertiary carbon are the same, the migration is simple.

Ex. 12. $\mathrm{R_2C(OH)\cdot CHPh(OH)\rightarrow R\cdot CO\cdot CHRPh}$, where $\mathrm{R=Me}^{(15)}$, $\mathrm{Et}^{(18)}$, $\mathrm{Pr}^{(18)}$, $\mathrm{Bu}^{(18)}$, $\mathrm{Bzl}^{(18)}$.

(b) *Case of selective migration.* When the tertiary carbon is substituted by two different groups, the migration takes place selectively. A close relation between polarity and selective migration has been often dealt with in the present and previous papers. But when dehydration is carried out substitutionally, it must be payed attention that the carbon which has been occupied by $\mathrm{SO_4H}$-group becomes strongly positive regardless of the original polarity, because the $\mathrm{SO_4H}$-radical deprives of the covalency electrons, when removed as ion. Therefore, if there exists sufficient difference of electro-negativity between the groups to be selected, the wandering group must be the one that is more negative.

Ex. 13.



$\mathrm{PhR\overset{+}{C}(OH)\cdot\overset{-}{C}HPh(OH)\rightarrow PhRC(OH)\cdot CHPh(SO_4H)}\underset{+\mathrm{R}}{\overset{-\mathrm{Ph}}{\rightarrow}}\!\!\rangle\mathrm{C(O\cdot)\cdot\underset{\cdot}{\overset{+}{C}}HPh\rightarrow R\cdot CO\cdot CHPh_2}$, where $\mathrm{R=Et}^{(10)}$, $\mathrm{Pr}^{(13)}$, iso-$\mathrm{Pr}^{(17)}$, $\mathrm{Bu}^{(13)}$, iso-$\mathrm{Am}^{(17)}$. In these cases, ketones $\mathrm{PhRCH\cdot CO\cdot Ph}$, are also formed, but only as by-products.); $\mathrm{Bzl}^{(17)}$.

On the other hand, if the polarity difference between the two groups is small, as is the case between alkyls, it is conceivable that the migration of the radical does not necessarily comply with the above rule. It is not a great error to assume that the stability of the union between these radicals and the tertiary carbon might play an important rôle in this case. If so, it must be the more positive group that migrates, for "a low degree of affinity for electron (i.e. of electronegativity) on the part of a radical results in instability of the bond which that radical may form with another radical or atom."*

Ex. 14. $\mathrm{RR'C(OH)\cdot CHPh(OH)\rightarrow R\cdot CO\cdot CHPhR'}$, where R′ is the more positive group, thus
$\begin{matrix}\mathrm{R} =\\ \mathrm{R'} =\end{matrix}\left\{\begin{matrix}\mathrm{Me}^{(19)},\\ \mathrm{Et},\end{matrix}\right. \left\{\begin{matrix}\mathrm{Me}^{(26)},\\ \mathrm{Pr},\end{matrix}\right. \left\{\begin{matrix}\mathrm{Me}^{(26)},\\ \text{iso-Pr},\end{matrix}\right. \left\{\begin{matrix}\mathrm{Me}^{(26)},\\ \mathrm{Bu},\end{matrix}\right. \left\{\begin{matrix}\mathrm{Et}^{(26)},\\ \mathrm{Bzl}.\end{matrix}\right. \left\{\begin{matrix}\mathrm{Pr}^{(26)},\\ \mathrm{Bu},\end{matrix}\right. \left\{\begin{matrix}\mathrm{Pr}^{(26)},\\ \mathrm{Bzl},\end{matrix}\right. \left\{\begin{matrix}\text{iso-Pr}^{(26)},\\ \mathrm{Bzl}.\end{matrix}\right.$
$\left(\left\{\begin{matrix}\mathrm{Pr}^{(26)},\\ \mathrm{Et},\end{matrix}\right. \left\{\begin{matrix}\text{iso-Pr}^{(26)}\\ \mathrm{Et}.\end{matrix}\right.\right)^{**}$

Ex. 15. $\mathrm{MeEtC(OH)\cdot CHAnis\,(OH)\rightarrow Me\cdot CO\cdot CHAnisEt}^{(25)}$.

Similarly we can explain the selective migration of such pinacones as $\mathrm{Me_2C(OH)\cdot CMeR(OH)}$, where $\mathrm{R=Et}^{(2)}$, $\mathrm{Pr}^{(22)}$, iso-$\mathrm{Pr}^{(22)}$; $\mathrm{Ph_2C(OH)\cdot CMeR(OH)}$, where $\mathrm{R=Et}^{(11)}$, $\mathrm{Bzl}^{(19)}$; and $\mathrm{MeEtC(OH)\cdot CMeEt(OH)}^{(16)}$, which have been dealt with as contradictions in the previous paper.

Conclusion.

Under the assumption that dilute sulphuric acid dehydrates catalytically, while the concentrated acid substitutionally, the mechanism of the

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* Kharasch and others, loc. cit.

**Exceptions.

rearrangements of all trisubstituted α-glycols can be interpreted causally from the stand point of the electronic conception of valence.

Semihydrobenzoin rearrangement occurs by the influence of dilute acid, when the tertiary hydroxyl has negative polarity and the hydrogen of the secondary hydroxyl is induced more positive than that bound to the secondary carbon.

Ex. $ArRC(OH){\cdot}CHPh(OH)$, $R_2C(OH){\cdot}CHPh(OH)$ and $Ar_2C(OH){\cdot}CHAnis(OH)$.

Vinyl dehydration takes place either (i) by dilute acid when the tertiary hydroxyl has negative polarity and the hydrogen combined to the secondary carbon is induced more positive than that of the secondary hydroxyl group; or (ii) by the concentrated acid when the tertiary hydroxyl has markedly negative polarity. Ex. (i) $Ar_2C(OH){\cdot}CHPh(OH)$, $R_2C(OH){\cdot}CHR'(OH)$; (ii) $Ph_2C(OH){\cdot}CHR(OH)$, $R_2C(OH){\cdot}CHR'(OH)$.

Semipinacolin rearrangement results either (i) from the dehydration of glycols with negatively polarized secondary hydroxyls by dilute sulphuric acid as well as concentrated; or (ii) by the action of the latter upon glycols with tertiary hydroxyls induced feebly negative. Ex. (i) $Bzl_2C(OH){\cdot}CHAr(OH)$; (ii) $RR'C(OH){\cdot}CHPh(OH)$ where $R = \text{or} \neq R'$. Such a glycol as satisfies the condition of semipinacolin rearrangement should have a strongly negative group, such as phenyl, in the secondary carbon in order to diminish the influence due to the strong positivity of the adjoining hydrogen. This requirement is nothing but the experimental law given by Lévy.*

The rearrangements of the glycols of the type, $RR'C(OH){\cdot}CHPh(OH)$, by concentrated sulphuric acid, are worthy of special mention, because they show plainly the close relation between the polarity and the mode of the rearrangements, making another maintenance to the electronic interpretation. Thus, if R′ is an alkyl, we have only semipinacolin rearrangement (Ex. 12 and 14); but if R′ is phenyl, the transformation is dependent on the electronegativity of the other radical R. Namely, the glycol, $RPhC(OH){\cdot}CHPh(OH)$, undergoes vinyl dehydration, if R is a strongly negative group such as Nap, Ph, or Me (Ex. 8); and if R is Bzl, a strongly positive group, semipinacolin rearrangement occurs (Ex. 13); while the both reactions take place at the same time, in a case when R is a group with weak or intermediate negativity such as Et, Pr, Bu or iso-Am (Ex. 13). We can find a plausible explanation of this in the competitive influences of polarity and of sterical factor.

It shall be here added that iso-butyl radical appears to be more negative than it is usually supposed, and it seems to be at least as negative as

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**Bull. soc. chim.*, [4] 33 (1923), 1655-66; ibid., [4] 39 (1926), 67-72.

methyl, since under the influence of concentrated sulphuric acid (iso-Bu) PhC(OH)·CHPh(OH), undergoes vinyl dehydration (Ex. 8), and (iso-Bu) RC(OH)·CHPh(OH), where R=Me(6) or Et(26), yields (iso-Bu)·CO·CHPhR by the migration of Me or Et radical (compare Ex. 14 and 15).

Migratory tendency of organic radicals is not a definite property as it has been supposed, but a function of their electronegativity, and the relation between them seems to be conditioned by two factors, that is, the attraction between the migrating groups and the atom to which the group passes, and the stability of the bond between the wandering group and the atom to be quitted. The first or the second factor is predominant, according to whether there exists sufficient difference of electronegativity between the groups undergoing selective migration (i) or not (ii). In the former case, the sence of polarity of the atom to which the group migrates, exerts a directive influence; thus, if the atom is positively polarized, the wandering group must be the one that is more negative (ia), and vice versa (ib). This conception has a powerful support in the actual existence of these two cases, (ia) and (ib), as is exemplified below. On the other hand, in the case where the second factor predominates, the migrating group is the one which is held with less stable bond, i.e. is the more electropositive group. Ex. (ia) Semipinacolic deamination of tertiary amino-alcohols, semihydrobenzoin rearrangement, semipinacolin rearrangements of RArC(OH)·CHPh(OH), where R=alkyl, (ib) Stieglitz's rearrangements: RR′R″C·NHOH, RR′R″C·NHCl or $RR'R''C\cdot NH_2 \rightarrow RR'C=NR''$, where the more electronegative halogenophenyls have less mobility than phenyl,* since the migration of a group takes place toward a negative atom, nitrogen. (ii) Semipinacolin rearrangements of RR′C(OH)·CHPh(OH), pinacolin rearrangements of $R_2C(OH)\cdot CR'R''(OH)$, where R′ and R″ are alkyls.

I beg to tender my sincere thanks to Prof. K. Matsubara for his kind inspection of this paper.

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