STUDIES ON MOLECULAR-REARRANGEMENTS OF α-GLYCOLS. IX. CONCLUSION (THE PINACOLINE REARRANGEMENT AS A METHOD OF ESTABLISHING RELATIVE ELECTRONEGATIVITIES OF ORGANIC RADICALS).

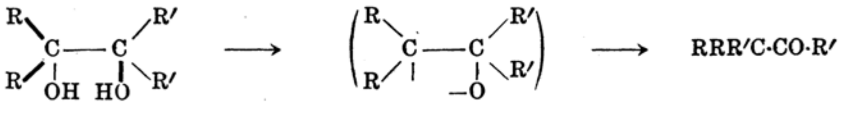
By Masao MIGITA.

Received December 3rd, 1932. Published January 28th, 1933.

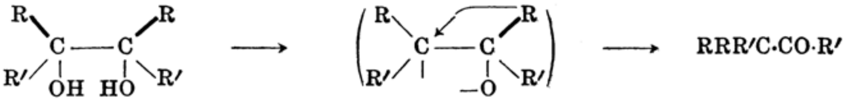
Migration Aptitudes of Organic Radicals. It was Meerwein(1) who explained the mechanism of pinacoline rearrangement by the theory of affinity requirement. His interpretation was originally intended to answer the question which hydroxyl group in *unsymmetrical* pinacone molecule is taken off, and it is impossible to explain why the radical with the larger affinity requirement has greater migration tendency in the rearrangement of a *symmetrical* pinacone.

---

(1) Meerwein, *Ann.*, **419** (1919), 121.



unsym. pinacone



sym. pinacone

where thick bars denote larger affinity requirement.

Therefore, Tiffeneau and Lévy(2) were obliged to conclude that a certain migratory aptitude is concerned to each radical, but this property is not necessarily concomitant with its saturation capacity. It must be specially mentioned here that they believed that each radical has its own migration tendency, since this idea has been and is still cherished by many organic chemists. Quite recently Bachmann(3) has stated in his studies on rearrangement of unsymmetrical aromatic pinacones as follows: "The series representing the relative migration aptitudes of the groups in symmetrical pinacones does not hold for the unsymmetrical pinacones. The series for the latter type of molecule may be expressed as follows: $C_6H_5 > CH_3C_6H_4 > CH_3OC_6H_4$. It is especially striking that the *p*-anisyl group, which in the symmetrical pinacone migrates nearly exclusively with respect to the phenyl group, migrates to a lesser extent than the phenyl group when the two groups are in the unsymmetrical molecule."

The reason why Bachmann considered the above result "especially striking" consists in the fact that he understands the migration aptitude as a definite property concerned to each radical.

The present author(4) has interpreted the pinacoline rearrangement from the electronic conception of valency any concluded that the order representing the migratory tendency of organic radicals is never constant but it may be reversed depending on the type of molecule subjected to rearrangement. By the author's theory it is quite possible to predict with certainty, the selective migration of radicals by pinacoline rearrangements irrespective of the type of pinacones. It is applicable not only to the rearrangements of pinacones, but also to those of tertiary

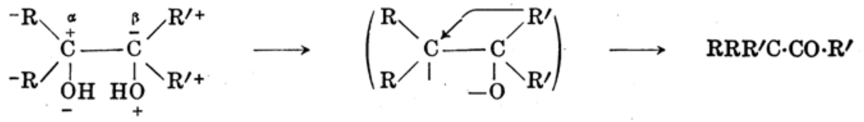
---

(2) Tiffeneau and Lévy, *Compt. rend.*, **176** (1923), 312.

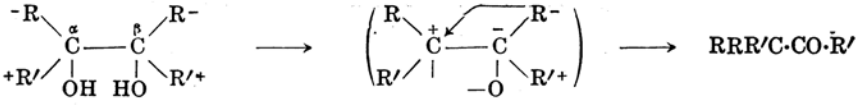
(3) Bachmann, *J. Am. Chem. Soc.*, **54** (1932), 2112–18.

(4) Migita, this Bulletin, **3** (1928), 315–6.

aminoalcohols(5) and of trisubstituted α-glycols(6). For example, the rearrangements of *unsymmetrical* and *symmetrical* pinacones will be reviewed here, which are expressed schematically as follows:



(I)		(II)		(III)



(IV)		(V)		(VI)

where R is more negative than R′.

Strictly speaking, it is not selective migration of radicals, but selective elimination of two hydroxyl groups that comes into question in the rearrangement of *unsymmetrical* pinacones of the type $R_2C(OH).CR'_2(OH)$. As for the selective elimination of these hydroxyl groups, the author has logically deduced that the more negatively polarized hydroxyl group, that is the one bound to carbon atom combined with the more negative groups, should be more ready to be eliminated(7). Thus, in formula I, the hydroxyl group attached to α-carbon atom will be more readily eliminated, which will result in formation of the fraction of molecule II. It is clear that the migration of a radical from β- to α-carbon atom in the fraction of molecule II can not be said selective, since the both radicals attached to β-carbon atom are the same. It appears, however, as if the more positive radical R′ migrates with respect to the more negative radical R, when the constitution of the pinacoline formed is simply compared with that of the original pinacone.

In the rearrangement of *symmetrical* pinacones the fraction of molecule shown in formula V will be produced intermediately, in which the α-carbon atom has extremely positive polarity, since it has been deprived of a part of its bond-forming electrons with the elimination of the hydroxyl group. Therefore, if one of the two groups attached to β-carbon atom migrates to α-carbon atom in order to make least the

---

(5) Migita, this Bulletin, **3** (1928), 313–314.

(6) Migita, ibid., **4** (1929), 57–65.

(7) Migita, ibid., **3** (1928), 312–313.

disturbance of the affinity, the group that wanders should be the one that is more negative. Thus migration of the more negative group will chiefly take place in the rearrangement of symmetrical pinacones.

It is concluded that the electronegativities of the substituents in the molecules exert directing influence on the selective elimination of the two hydroxyl groups in the rearrangement of unsymmetrical pinacones and on the selective migration of radicals in the case of symmetrical pinacones.

Relative Electronegativities of Organic Radicals. If migration of radicals in the rearrangement of a pinacone can be predicted by their electronegativities, as shown above, conversely the relative electronegativities of any two radicals R and R′ can be determined from the rearrangement products of the symmetrical or unsymmetrical pinacone containing the two radicals in question. For this purpose, it is sufficient to analyse organic acids produced by the hydrolysis of the rearrangement products. Thus a pinacoline rearrangement offers a simple method to compare electronegativities of organic radicals.

An interesting method to determine relative electronegativities of organic radicals has been given by Kharasch and Marker(8), in which mercury is coupled with two organic radicals R and R′ and the resulting compound is treated with hydrogen chloride. The reaction runs as follows:

$$RHgR' + HCl \rightarrow RH + R'HgCl.$$

It is plausible to assume that the more electronegative of the two radicals R and R′ combines with H^+ to form corresponding hydrocarbon.

Though this method exceeds the pinacoline method in its theoretical interest, it has some disadvantages for practical purpose. Firstly it is generally not so easy to prepare an organomercuric compound containing two given radicals as to prepare a pinacone with the same radicals, and secondly isolation and identification of a mixture of organomercuric chlorides will be in most cases more troublesome work than in the case of a mixture of organic acids(9).

In the pinacoline method the pinacones of either symmetrical or unsymmetrical type which contain the two radicals to be compared may

---

(8) Kharasch and Marker, *J. Am. Chem. Soc.*, **48** (1926), 3130.

(9) Analysis of a mixture of organomercuric chlorides by its mercury content and that of organic acids by the silver value are applicable only when no high degree of accuracy is demanded.

be used(10), but the symmetrical pinacone is preferable to the other on account of its easiness of preparation. It is especially so when the electronegativities of aromatic radicals are compared, since in this case a simple method is available as described below. Under certain conditions, we may obtain pinacolines, instead of pinacones, when certain aromatic ketones are reduced by glacial acetic acid and zinc dust. It has been proved experimentally as well as theoretically that this direct pinacoline formation from a ketone takes place when both radicals attached to carbonyl group are of high electronegativities(11). Therefore, if the ketone RCO.R′ is reduced to pinacoline, while the ketone RCO.R″ to pinacone, we can conclude that R′ is more negative than R″. Thus, we can compare the relative electronegativities of aromatic radicals simply from the reduction products of two suitable ketones.

In the foregoing works the author has attempted to compare electronegativities of several highly negative aromatic radicals by pinacoline method and obtained the following series,

$$C_2H_5OC_6H_4 > CH_3OC_6H_4 > \alpha\text{-}C_{10}H_7 > \beta\text{-}C_{10}H_7\,,\ C_6H_5C_6H_4\,,$$

which contains some supplements as well as confirmations to the series of electronegativities given by Kharasch and colaborators. Hithertofore, *p*-anisyl has been considered to be the most electronegative radical but it is found that *p*-ethoxyphenyl radical is by far more negative. β-Naphthyl radical is proved to be more positive than α-naphthyl radical and to rank nearly with diphenylyl radical with respect to its negativity.

Dissociation of Pinacones. The criterion of the stability of a carbon-to-carbon bond is the affinity of the bound radicals for the binding electrons. When the electrons are closely held by both carbon nuclei, the bond is stable; when they are displaced away from one or both nuclei the bond is unstable. Therefore, we can distinguish two cases in unstable linkages between two carbon atoms, thus:

1. Linkage between two radicals of very slight electronegativities, in this case the binding electrons are displaced away from both carbon nuclei.

2. Linkage between an extremely electronegative organic radical and a weakly electronegative one, in which the bond-forming electrons are held at a distance from one nucleus.

---

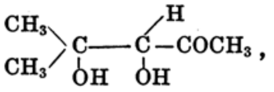
(10) It must be remembered that the relation between migration aptitude and electronegativity is reversed in these two cases.

(11) Migita, this Bulletin, **7** (1932), 335, 342, 380.

Dissociation of hexa-aryl ethanes into free radicals and high reactivity of chlorine atom in triarylmethyl chlorides may be cited in illustration of the cases 1 and 2 respectively.

Aromatic pinacones bear close resemblance to hexa-aryl ethanes with respect to the negativities of substituents, and their molecules have unstable linkage of the first kind between the two carbon atoms in chain. Therefore they are naturally assumed to dissociate with production of free radicals under certain conditions, as in the case of hexa-aryl ethanes. This assumption has been confirmed experimentally⁽¹²⁾ by the fact that iodomagnesium ketyl radicals with tervalent carbon atoms, RR'Ç.OMgI, are formed when aromatic ketones are reduced by binary mixture of magnesium and its iodide in benzene-ether solution. The formation of free ketyl radicals is recognized by the development of intense colourations, sensible toward oxygen, in the process of reduction.

Besides this, aromatic pinacones undergo another kind of dissociation, that is scission into ketones and carbinols, which is also attributable to the presence of unstable linkage in the molecule. According to literature, the dissociation of aromatic pinacones into ketones and carbinols takes place nearly exclusively at their melting points, tetra-*p*-bromobenzophenone⁽¹³⁾ is the only pinacone that undergoes rearrangement and this sort of dissociation simultaneously by the action of acetyl chloride. Being interested in this singular instance, the author has carried out close experiment with tetra-*p*-methoxy-benzopinacone under the same conditions, but dissociation into ketone and carbinol could not be observed.

The author has observed that the dissociation into ketone and carbinol takes place not only in aromatic pinacones, but also in αα-dimethyl-β-acetyl glycol,  $(CH_3)_2C(OH)-CH(OH)-COCH_3$, an aliphatic glycol containing unstable linkage of the second kind, and that with far greater facility⁽¹⁴⁾.

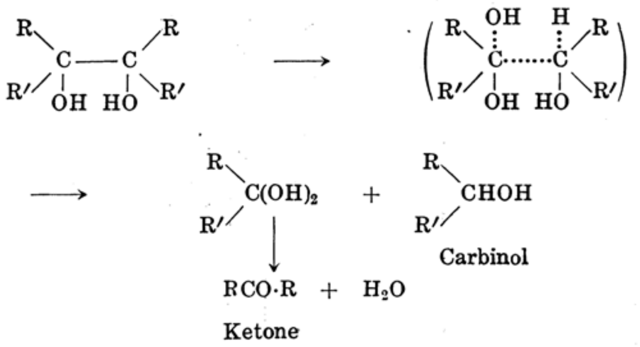
The mechanism of dissociation into ketone and carbinol can be interpreted as follows: In the first stage of the reaction, addition of water takes place at the two adjacent carbon atoms with unstable linkages, which weakens more the bond between these carbon atoms and results in scission of the molecule at this point.

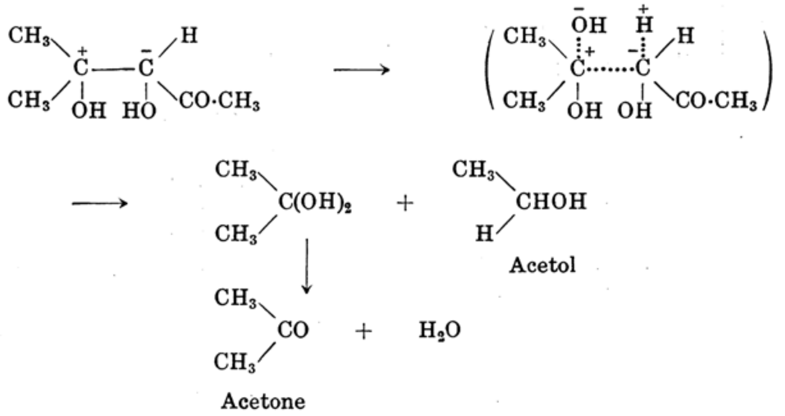
---

(12) Gomberg and Bailar, Jr., *J. Am. Chem. Soc.*, **51** (1929), 2229.

(13) Montagne, *Rec. trav. chim.*, **43** (1924), 126–142.

(14) Warming with dilute acid or alkali is sufficient to cause the scission of the glycol. Migita, this Bulletin, **4** (1929), 226–7.

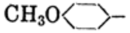
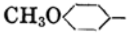
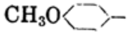
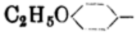
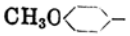
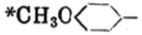
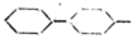
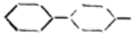
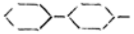
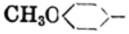
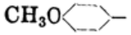
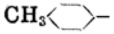
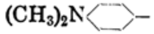
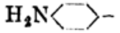
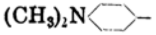
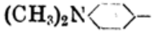




Addition of water is naturally expected to occur easier when the polarities of the two carbon atoms are of different signs than when they are same. This is the reason why dimethyl-acetyl glycol with the second kind of unstable linkage exceeds aromatic pinacones with the first kind of unstable linkage in its facility of dissociation into ketone and carbinol.

Reduction of Aromatic Ketones with Highly Negative Groups. Aromatic pinacones are generally obtained by reducing corresponding ketones (i) with zinc dust and glacial acetic acid, (ii) with absolute alcohol under direct sunlight or (iii) with the binary mixture of magnesium and magnesium iodide in benzene-ether solution. The author has reduced several aromatic ketones with highly negative groups by these methods and found that the products are not necessarily pinacones, but they may be pinacolines, carbinols or hydrocarbons under certain conditions (See the Table below).

Reduction of some Aromatic Ketones with Highly Negative Radicals.

Ketone, RCO·R′		Reducing Agents.			
		Glacial acetic acid and zinc dust.		Absolute alcohol under direct sunlight.	Magnesium iodide and magnesium.
R·	R′ ·	At room temp.	At higher temp.		
		$R_3C{\cdot}CO{\cdot}R$	$R_3C{\cdot}CO{\cdot}R$	$R_2C(OH){\cdot}C(OH)R_2$	Rosinous matter.
		——	$RR'_2C{\cdot}CO{\cdot}R$	$RR'_2C{\cdot}CO{\cdot}R$	——
		$RR'C(OH){\cdot}C(OH)RR'$	$R_2R'C{\cdot}CO{\cdot}R'$	Not reduced.	——
		$RR'C(OH){\cdot}C(OH)RR'$	$R_2R'C{\cdot}CO{\cdot}R'$	Not reduced.	——
		$RR'CHOH$	$RR'CH_2$	Not reduced.	Pinacone ?
		$RR'CHOH$	$RR'CH_2$	——	——
		$RR'CHOH$	$RR'CH_2$	Not reduced.	$RR'C(OH){\cdot}C(OH)RR'$
		——	$R_2C(OH){\cdot}C(OH)R_2$ a)	$R_2C(OH){\cdot}C(OH)R_2$ b)	$R_2C(OH){\cdot}C(OH)R_2$ c)
		$RR'C(OH){\cdot}C(OH)RR'$ d)	$R_2R'C{\cdot}CO{\cdot}R'$ e)	——	$RR'C(OH){\cdot}C(OH)RR'$ d)
		$RR'C(OH){\cdot}C(OH)RR'$ d)	$R_2R'C{\cdot}CO{\cdot}R'$ d)	——	$RR'C(OH){\cdot}C(OH)RR'$ d)
		——	$RR'C(OH){\cdot}C(OH)RR'$ f)	——	——
		——	R_2CH_2 g)	——	$RR'C(OH){\cdot}C(OH)RR'$ c)

* Unpublished.
a) Zagumenni, *Ber.*, **14** (1881), 1402.
b) Ciamician and Silber, *Ber.*, **33** (1900), 2912.
c) Gomberg and Bachmann, *J. Am. Chem. Soc.*, **49** (1927), 249, 254.
d) Bachmann and Moser, *J. Am. Chem. Soc.*, **54** (1932), 1126.
e) Tiffeneau and Orékhoff, *Bull. Soc. chim.*, **37** (1925), 430.
f) Willstätter and Goldmann, *Ber.*, **39** (1906), 3768.
g) Votoček and Krauz, *Ber.*, **42** (1909), 1602.

(i) *Reduction by Zinc Dust and Glacial Acetic Acid.* Aromatic ketones containing highly negative groups are generally reduced by zinc dust and acetic acid to pinacones at ordinary temperature and pinacolines at higher temperature; however, if the negativities of the groups are extremely high, pinacolines are formed even at ordinary temperature as in the case of di-*p*-methoxy-benzophenone.

α-Naphthyl-diphenylyl and β-naphthyl-diphenylyl ketones and αβ-dinaphthyl ketone give carbinols at room temperature and hydrocarbons at higher temperature. This behaviour is considered to concern with sterical problem, rather than with negativity problem.

(ii) *Reduction by Absolute Alcohol under Direct Sunlight.* This method seems inapplicable to ketones which are difficultly soluble in alcohol. It is highly interesting that *p*-methoxy-*p'*-ethoxy-benzophenone is not reduced to pinacone but to pinacoline by this method, while di-*p*-methoxy-benzophenone gives pinacone under the same conditions. We can see, here also, the influence of highly negative substituents on a pinacone in its reactivity.

(iii) *Reduction by Magnesium and Magnesium Iodide.* Reduction by this method has been reported not only to give an excellent yield such as from 75 to 100 percent, with many aromatic ketones, but also to be successful to the ketones to which all other methods fail. The present author has also experienced that β-naphthyl-diphenylyl ketone is reduced to corresponding pinacone only by this method. However, this method seems to give less satisfactory results in the reduction of ketones containing *p*-anisyl radical, for example, Bachmann and Moser(15) observed that 4-methoxy-, 4-methoxy-4'-methoxy-, and 4-methoxy-4'-phenyl-benzophenones were reduced to corresponding pinacones with the yields of 45, 2 and 35% respectively. The author did not succeed in reducing di-*p*-methoxybenzophenone by this method.

In conclusion, the author begs to tender his sincere thanks to Prof. K. Matsubara for his kind advices and encouragements throughout this work.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

---

(15) Bachmann and Moser, *J. Am. Chem. Soc.*, **54** (1932), 1126.