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Mechanism of 1,2-shift through p-complex transition state

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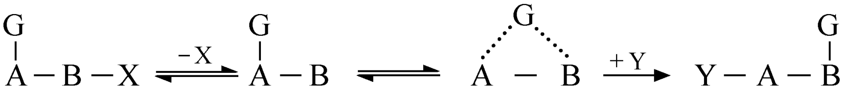
Abstract A systematic calculation of the potential curves or surfaces for 1,2-shift has been realized by using MNDO or other models in MOPAC programs. By referring to the previous authors' viewpoints, the 1,2-shift can be divided into two categories. 1,2-electron-deficient shift is that the electronic configuration of the atom which accepts the migrating group is a cation or an electron-deficient atom, and 1,2-anion shift is the one that the accepted atom of the migration group is a negative ion. In terms of the experimental facts and the calculation of the potential surfaces, in electron-deficient shift such as Beckmann or Baeyer-Villiger rearrangement, the migration occurs through a transition complex formed between the π-bond and the cation or electron-deficient migrating group, but in anion shift such as Wittig or Stevens rearrangement, the electron pair in π-orbit excites at first to π^* orbit, and then the migration occurs through the new formed complex between the anion migration group and the vacant π orbit. The above mechanisms explain reasonably the intramolecular properties, the configuration retentions of the migration group, and the corresponding migratory aptitudes of the two type 1,2-shifts. The partial and less important free radical reaction of 1,2-anion shift has been explained by the π-complex mechanism too.

Keywords: 1,2-shift, rearrangement, MNDO, potential surface, p-complex, Wittig rearrangement.

The combination of quantum chemical calculation and summarization of experimental facts displays great motivation in explanation of the scientific rules. Di-region theory put forward by Dai Qianhuan through theoretical calculation[1] explains successfully the mechanism of chemical carcinogenesis outstanding for a long time. Recently, di-region theory has got convincing evidences by the experiments of molecular biology[2,3]. Based upon a systematic quantum chemical calculation on electrophilic additions worked out by computer recently, Dai Qianhuan put forward the d-π excited hybridization donor-acceptor complex mechanism[4—6], which explains successfully the rules of the mechanism, stereo-selectivity and regio-selectivity of electrophilic addition reactions, and promotes the research of the mechanism on electrophilic additions to a new level of quantum mechanics. In this paper, we conclude through a large quantity of systematic quantum chemical calculation on computer that the important rearrangement reaction of 1,2-shift is not a concerted one but proceeds through a π-complex transition state.

1,2-shift is one of the most important types in rearrangement reactions, which includes many important reactions in theoretical and practical aspects. There are controversies in molecular mechanism of 1,2-shift, and it would merit more attention. The general equation of 1,2-shift may be summarized as follows:



$$\overset{\overset{G}{|}}{A}-B-X \xrightleftharpoons{-X} \overset{\overset{G}{|}}{A}-B \rightleftharpoons \overset{\cdot\cdot\cdot G\cdot\cdot\cdot}{A\;-\;B} \xrightarrow{+Y} Y-A-\overset{\overset{G}{|}}{B} \qquad (1)$$

where G is the migrating group including alkyl, aryl, alphyl group or hydrogen atom, A is a group in general by using carbon atom as its center, B may be carbon, nitrogen or oxygen atom or the corresponding group, X is the leaving atom or group, and Y is the atom or group which may be identical to X or not.

It will be noted from the following paragraphs that although some individual reactions of 1,2-shift have been discussed with theoretical calculation, the systematic treatment of 1,2-shift with calculation quantum chemistry has not been undertaken as yet. The aim of this paper is to discuss systematically the molecular mechanism of 1,2-shift by combining closely the experimental facts and theoretical potential curves or surfaces obtained from MNDO calculation or other molecular models of MOPAC programs. Other than the non-empirical *ab initio* system, the semi-empirical models, EHMO, MNDO, AM1 and PM3 recommended by MOPAC are still useful in advanced calculations, and their virtues and defects are decided by different fields of application regardless of the sequence of their development[7,8]. Theoretical chemists would forgive this author his superfluous words which might be necessary only for some experimental organic chemists.

The experimental facts of 1,2-shift may refer to March’s[9] or Lowry and Richardson’s book[10]. The original materials will not be cited unless it is really necessary. By referring to the previous authors’ classification, in terms of the characteristic of the electron configuration in valence shell of the accepted atom, i.e. atom B in eq. (1), for the migrating group, the 1,2-shifts may be divided into two categories. The 1,2-shift can be called 1,2-electron-deficient shift if before the rearrangement, the atom B is a cation or an electron-deficient species with only six electrons in its valence shell, and 1,2-anion shift is named if atom B is an anion species before the rearrangement.

1 1,2-Electron-deficient shift

1,2-Electron-deficient shift in which the centered atom in B has the positive charge is called cation 1,2-shift. In the category of cation 1,2-shift, there are pinacol, Wagner-Meerwein and Demjanov rearragements with a carbon atom as the charged center; Beckmann and Stieglitz rearrangements have nitrogen atom center and an oxygen atom is the center for Baeyer-Villiger and Hock rearrangements. If the centered atom in B is an electron-deficient species with only six electrons in its valence orbit, this type of 1,2-shift is an electron-deficient 1,2-shift in narrow sense. In electron-deficient 1,2-shift, the examples with electron-deficient carbon atom are Wolf rearrangement in Arndt-Eistert synthesis as well as the Fritsch-Buttenberg-Wiechell rearrangements, and the examples with electron-deficient nitrogen atom are Hoffmann, Curtius and Losson rearrangements. The variations of the electronic configuration in the course of rearrangement for both subclass categories of 1,2-electron-deficient shift are analogous to each other. It has been evidenced with experiments that all the above-mentioned rearrangements are strictly intramolecular properties, the cross over reaction between inter-molecules in 1,2-electron-deficient shift, has not been observed in all the cases and the configuration of the migratory group is always kept with almost 100% retention. In general, the migratory aptitudes of G in all 1,2-electron-deficient shifts are decided by the cation stabilities of the migrating groups.

The dynamic behavior of 1,2-shift can be classified into two typical conditions based upon experiments. In asynchronous process, leaving group X leaves completely from B, and a cation or an electron-deficient species is formed on the center atom of B at first, then the rearrangement occurs. For example, the configuration of carbon atom on B in Demjanov rearrangement of threo-1-amino-1-phenyl-2-p-methyl-phenyl-propan-2-ol by reaction with nitric acid is non-stereo-selectivity in the reaction course because of the free rotation around the carbon-carbon single bond between 1- and 2-positions. The distribution of two isomers is determined by conformational stability of the intermediate cation, and the rearrangement gives 58% retention and 42% inversion on configuration of carbon atom in B. In another synchronous process, the leaving of X and the migration of G occur synchronously. For example, the center oxygen atom with high electronegativity in Baeyer-Villiger rearrangement is very difficult to form a stable cation, and in general this reaction occurs concertedly. The property of the rearrangement may be situated at an intermediate state between the two typical conditions depending upon solvent polarity, character of the leaving group and stability of the cation. The reaction velocity of 1,2-electron-deficient shift is determined by the step of the migration of group G regardless of whether the reaction is an asynchronous or a synchronous process, implicating that both conditions have a common mechanism.

The configuration retention in 1,2-electron-deficient shift as a two-electron $4n+2$ process, is consistent outwardly with orbital symmetrical conservation rule, but inwardly it is not a concerted pericyclic reaction because it requires the definite and heterogeneous charge distribution on G, A and B groups during its transition state. The migratory aptitudes of G group are decided by the stabilities of G as a cation or an electron-deficient species, and it shows that the center atom of G has an electron-deficient vacant orbit which can be migrated by complexing with the newly formed π-bond between A and B. For example, in Beckman rearrangement of (E)-substituted acetophenone oximes in concentrated sulfuric acid, the reaction velocities are correlated well with σ^+ constants of the substitutes, which uncovers the cation characteristic of migratory group G. According to this model, a potential surface for Beckmann rearrangement of acetophenone oxime is obtained through MNDO calculation. In general, Beckmann rearrangement is a synchronous process and obeys the stereo-selectivity of anti-migration rule, i.e. the migratory group G in anti-position of leaving group X is moving synchronously during the leaving of X. However, in Beckmann rearrangement of diaryl-ketone oxime such as (E)-ArAr$'$ C$=$NOH in concentrated sulfuric acid, because of high polarity of solvent and conjugated stability of the nitrenium ion, ArAr′ $C{=}N^+$, by both aryl groups, the reaction takes an asynchronous manner and non-stereo-selectively gives both isomers. The calculation of potential surface for Beckmann rearrangement, taking $(CH_3)_2C{=}N^+$ ion as the starting point to simulate the above asychronous process, was carried out by letting ion plane overlap *YZ* plane, the center of C═N bond coincides with origin, and the moving position of CH_3 in migratory process is determined by automatic optimization with MOPAC 6.3 and MOPAC97. The obtained potential surface is illustrated in fig. 1(a), where *Z* axis is the energy, *Y* is the distance from origin and *X* is the angle between the center of carbon atom and *YZ* plane. The top part of this potential surface with its enlarged scale is illustrated in fig. 1(b). It is shown by calculation that CH_3 group migrates around a circular curve approximately, and steps over a barrier just at the center of C═N bond. The minima in enrgy valley are always situated on the *YZ* plane, which reflects the control effect to the migratory group by perpendicular π-bond electron cloud to *XY* plane. Before the calculation, by giving a definite positive charge to CH_3, a definite triple bond on C—N is formed. The potential surface of Beckmann rearrangement obtained from MNDO calculation is consistent with the mechanism that 1,2-electron-deficient shift goes through a π-complex formed between G^+ and the newly formed π-bond.

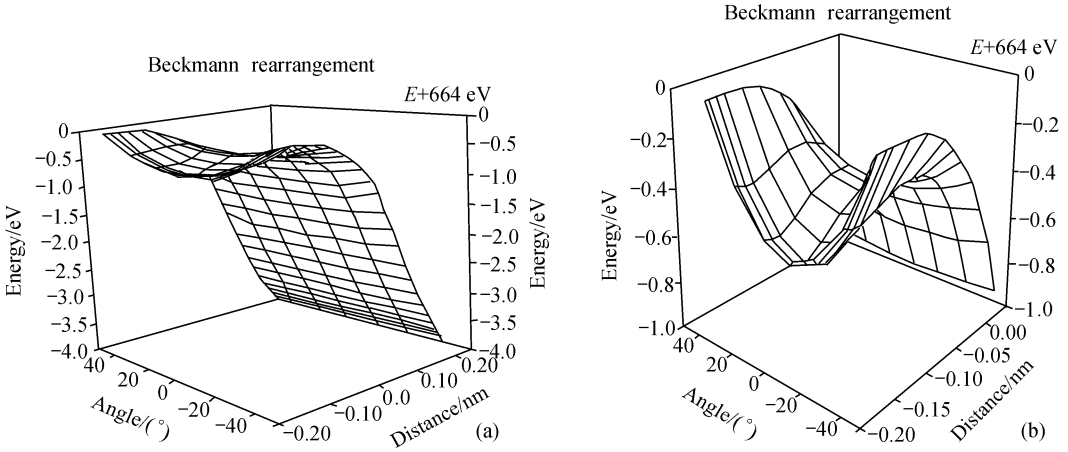


Fig. 1. (a) Potential surface of a typical Beckmann rearrangement by MNDO model. (b) The top part of the potential surface with enlarged scale.

Further evidence for the importance of π-bond formation has been got in the potential surface obtained by MNDO calculation of the migration of phenyl group in 2-phenylethyl cation, an intermediate species of Wagner-Meerwein or Demjanov rearrangement. The result is illustrated in fig. 2, where the angle is in degree for benzene ring out of perpendicular to C—C bond. It is shown by calculation that phenyl group migrates strictly along C—C bond and the benzene ring plane always moves perpendicularly to C—C bond, and the rearrangement is realized through the formation of a phenonium ion as evidenced by the experiment. The potential curve of rearrangement of 2-phenyl-1,2-dimethyl-ethyl cation by MNDO calculation is illustrated in fig. 3, where the benzene ring is assumed to be always perpendicular to C—C bond, and the result is analogous to the rearrangement of 2-phenylethyl cation. Dewar indicated[11] that the vacant orbit of phenyl cation forms an acceptor bond with π-bond and the occupied p orbit perpendicular to benzene ring forms a donor bond with π^*-bond, so the phenonium ion is very stable as illustrated in the minimums of figs. 2 and 3 because of the formation of an acceptor-donor bond. These calculations verify further the mechanism of π-complex transition state for 1,2-electron-deficient shifts.

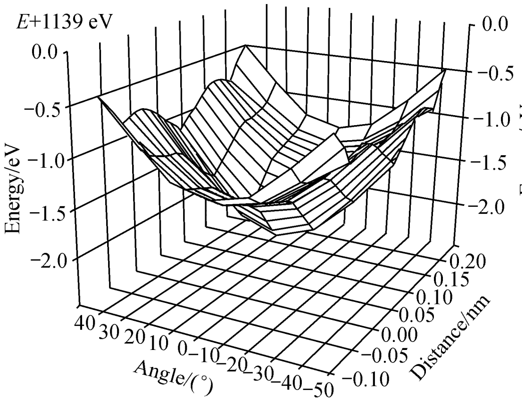


Fig. 2. Potential surface of a typical Wagner-Meerwein rearrangement by MNDO.

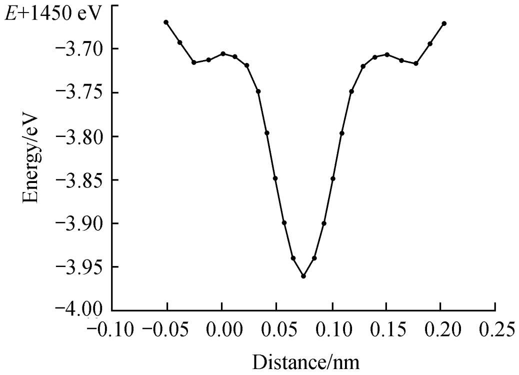


Fig. 3. Potential curve of phenyl migration in 2-phenyl-1,2-dimethyl-ethyl cation.

Baeyer-Villiger rearrangement is a synchronous process as evidenced by ^{14}C isotop labeling experiment, i.e. the migration of the group and the leaving of carboxylate ion occur synchronously. The reaction velocities for rearrangements of substituted acetophenones by oxidation with trifluroperoxyacetic acid with $r = -1.45$ are correlated well with s values, showing that the phenyl groups under migration develop a cation property in certain degree. Two potential curves of MNDO calculations for benzophenone by oxidation with peroxyacetic acid are illustrated in fig. 4, one with the higher initial energy is calculated according to a synchronous course and the other curve is obtained in terms of an imaginary asynchronous process. In practice, it is possible that the reaction overleaps the barrier near the cross point of the two curves to realize the rearrangement. So the MNDO calculations for Baeyer-Villiger rearrangement are consistent with its synchronous property concluded by dynamical experiment.

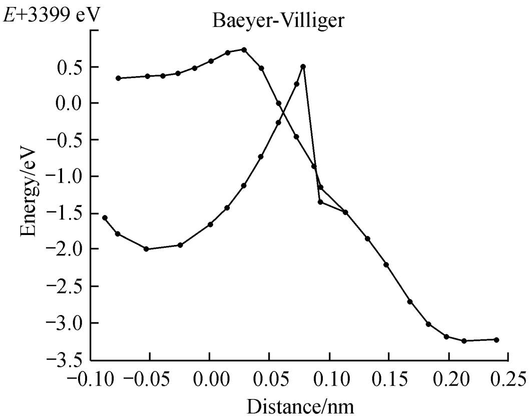
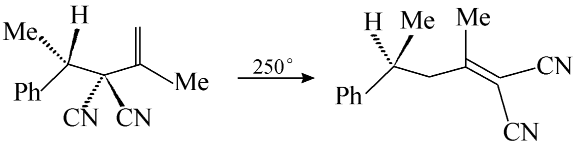


Fig. 4. Potential curves of MNDO for reaction of benzophenone with peroxyacetic acid.

It is a common phenomenon that a cation with vacant orbit can be migrated by complexing with a π-bond or a π-system. For example, the so-called [1,3]-sigmatropic thermal shifts illustrated in eqs. (2) and (3) are 4*n* process with just 4 electrons to join the reaction, however, both of which violate the predictions of configuration inversion based upon orbital symmetric conservation rule, but give products with configuration retention for most part of product[13]. It is shown that both reactions are not concerted pericyclic shifts but the rearrangements through a cation by complexing with a 4-electron conjugated π-system. It may be expected that many 1,3-shifts of a 4-electron process with configuration retention will be discovered in the future.



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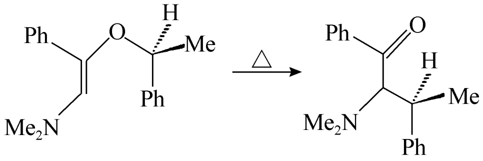


(3)

Favorskii rearrangement of α-haloketone under the reaction with a base of alkyloxy, hydroxyl anion or sodium amide forms ester, acid or amide, which according to common classification may be included in anion rearrangement category because the first step is the formation of an anion by reaction with a base. In practice, the key step of Favorskii rearrangement which determines the reaction velocity is the formation of a cation on α-carbon during the leaving of halogen anion, then the formed electron-deficient species like a carbene migrates along the newly formed π-bond to realize the rearrangement. So, based upon the electron configuration of the key step, Favorskii rearrangement may be classified as a 1,2-electron-deficient shift. By using chloroacetone as an example, put the carbon atom of carbonyl group in $^{-}CH_2COCH_2Cl$ on the origin, let the carbene analogue $:CH_2$ move along newly formed π-bond between C—C of a ketene analogue species. In terms of the automatic optimization of MNDO calculation, $:CH_2$ migrates approximately along a circular curve. The calculated potential curve is illustrated in fig. 5, and it has a very deep energy valley and

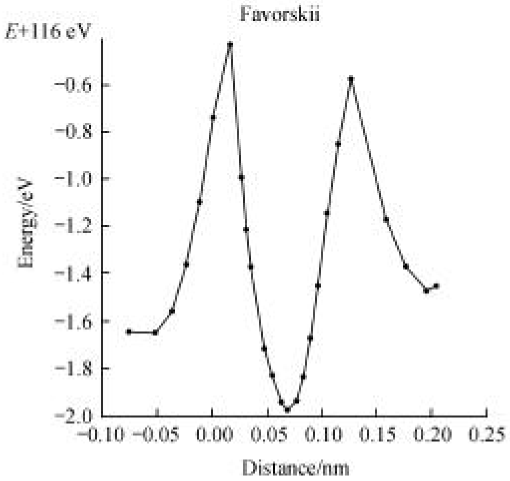
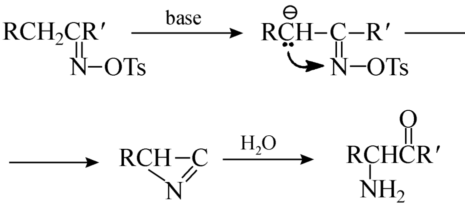


Fig. 5. MNDO potential curve of a typical Favorskii rearrangement.

implicates that an intermediate compound of cyclopropanone must form there, which is completely consistent with the experimental fact. Obviously, the theoretical π-complex model for Favorskii rearrangement shows that MNDO calculation can match well with the experimental facts.

By referring to the new classification of Favorskii rearrangement, Neber rearrangement can be included as a 1,2-electron-deficient shift too. As in eq. (4) of Neber rearrangement, p-toluenesulfonate of a ketone oxime under the effect of a base forms a carbanion.



(4)

The rearrangement is an asynchronous process because the C═ N^+ cation will be formed preferentially based upon the conjugated effect of negative charge, which is different from Beckmann synchronous process with the migration of an antigroup, showing a non-stereo selectivity manner. Analogous to Beckmann rearrangement, then the carbene species migrates along the formed π-bond to give an intermediate aza-cyclopropene which reacts with water to form an aminoketon.

The immigrating groups around the A-B bond in eq. (1) are always coplanar in the transition state of all the calculated 1,2-shifts mentioned above, which shows that a transient π-bond as well as its π-complex with the migrating electron-deficient species should be formed. Many experimental facts show that the coplanar configuration decided by a π-bond is necessary in the transition state of 1,2-shift. For example, the inter-molecular characteristic of hydrogen 1,2-shift in 1-methyladamantyl-2-cation and the pinacol rearrangements of the two isomers of 1-phenyl-4- tert-butyl-trans-cyclohexa-1,2-diol to form identical products verify the prerequisite of the coplanar arrangement, i.e. the π-complex formation in the transition state of 1,2-electron-deficient shift[10].

It is well known that in benzilic acid rearrangement, the base is combined with the carbon in a carbonyl group, so an electron-attraction group on benzene ring will promote the reaction. However, the successive process would be that a phenyl cation migrates along the π-bond of a ketene species through the π-complex, so according to the mechanism of this key step, the benzilic acid rearrangement is a sort of 1,2-electron-deficient shift too. Recently, Rajyaguru et al.[12] discussed the benzilic acid rearrangement with MNDO calculation. Although the formation of a π-complex is not felt by them, their results are not in contradiction to our conception.

2 1,2-Anion shift

According to our classification, Favorskii and Neber rearrangements are not included in anion or electrophilic shift as in common practice, but classified more reasonably as electron-deficient shifts due to the electron-deficient character on the acceptor atom of the migrating group. Therefore, the typical 1,2-anion shift includes only Wittig, Stevens, sulfur-ylid Stevens, Meisenheimer and Grovenstein-Zimmermann rearrangements[9,10,14]. Among them, Wittig and Stevens rearrangements have undergone more thorough research. In both cases, there are almost no cross-over product with isotope labeling, configuration retention of chiral migrating group in most part and other experimental facts show that both rearrangements are intramolecular reactions in the majority. However, in both rearrangements, a small quantity of cross-over products and racemic products have been observed, and the appearances of CIDNP spectrum verify the presence of free radicals in both reactions. In Wittig rearrangement, obviously, the small quantitative aldehyde by-product originates from the small part of free radical reaction identified by CIDNP spectrum. The puzzling characteristics of both rearrangements, i.e. a three-center bond could accommodate four electrons or a carbon atom could accept ten electrons, inhibit the research on these reactions. A concerted mechanism for both rearrangements is impossible, in which configuration retention of a four-electron process is inconsistent with a $4n$ pericyclic reaction of configuration inversion. It is surprising that the previous authors did not use a quantum mechanic model but a classic conception instead to explain the mechanism of 1,2-anion shift.

According to our idea, it is possible that the four electrons would occupy π and π^* orbits of the newly formed π-bond in C—O and C—N of Wittig and Stevens rearrangements, respectively. The energy of two electrons occupying an excited π^* orbit is much lower than that of these two electrons occupying an excited σ^* orbit. Under the effect of base, the electron pair in formed anion excites up to π^* orbit and the migrating group G as an anion moves along vacant π-orbit by complexing with it, i.e. in the migrating course, occupied sp^3 hybridation orbit always overlaps the vacant π-orbit. This π-π^* complex model explains reasonably the main characteristics of intramolecule and configuration retention of 1,2-anion shifts. The electron in π^* orbit in the molecule with higher energy may be excited up to σ^* orbit because of the allowance process based upon symmetric consistency between π^* and σ^* orbits. After σ^* orbit of G accepting the excited electron, G will be separated from the complex to show a free radical character, and the racemization or the formation of cross-over products will occur if radical $G^\bullet$ combines again with $A\text{-}B^\bullet$ free radical, and the $A\text{-}B^\bullet$ radical may form an aldehyde during the reaction. A potential surface of Wittig reaction with methylbenzyl ether is illustrated in fig. 6 by MNDO calculation according to the above model. It is assumed that an α-carbanion of benzyl group has been formed already. Put the center of oxygen atom on the origin. Letting symmetric plane of the π and π^* bonds overlap YZ plane, the migrating positions of CH_3^- group and orientations of other groups may be determined by the automatic optimization of the program. It may be noted that the CH_3^- group migrates along an energy valley to realize the rearrangement by overleapping a barrier, and the obtained potential surface by MNDO calculation verifies that the 1,2-anion rearrangement goes through a π-π^* complex transition state in which both π and π^* orbits are occupied.

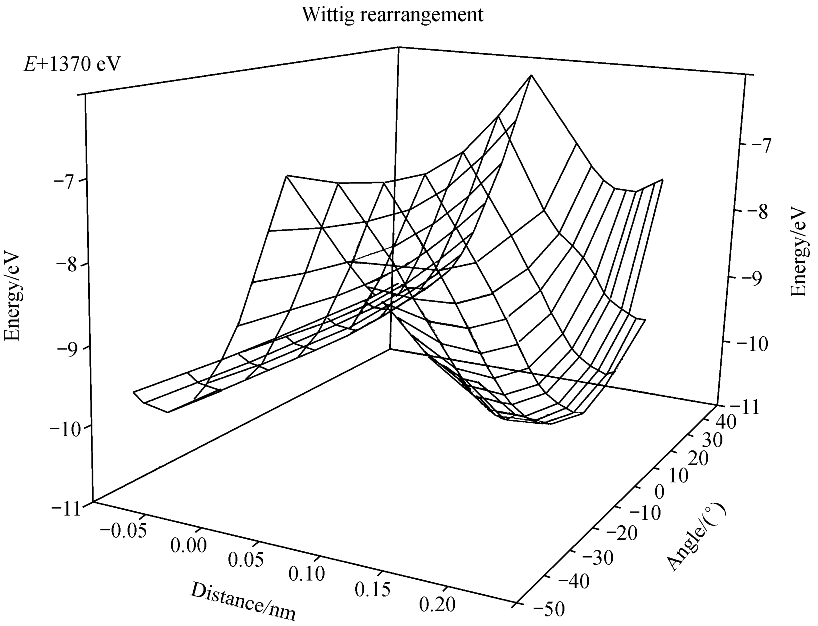
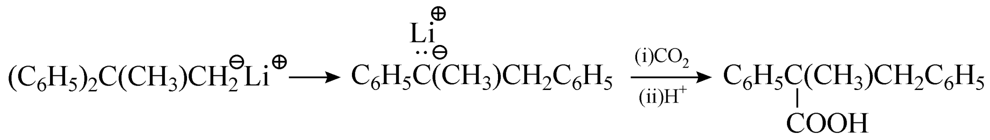
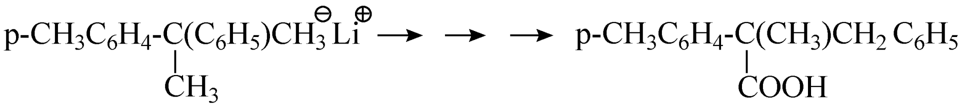


Fig. 6. Potential surface of a typical Wittig rearrangement by MNDO calculation.

A free radical pair mechanism has been proposed to explain Wittig and Stevens rearrangements, which considered that a free radical pair surrounded by a "solvent cage" would be formed between both free radicals of migrating group and original molecular skeleton in order to explain the intramolecular character and configuration retention of these reactions. However, the "solvent cage" effect appears only in a non-polar solvent and in general is not a main route of a free radical reaction, and it would be something farfetched to explain a main reaction in polar solvent condition with the "solvent cage" effect. The major basis of free radical mechanism is that in Wittig and Stevens rearrangements, the migrating aptitudes of the group are in the following sequence, $C_6H_5CH_2\text{—} \cong CH_2\text{=}CHCH_2\text{—}> CH_3CH_2\text{—} \cong CH_3\text{—}> C_6H_5\text{—}$. So some authors considered that it would be a sequence of the stabilities for free radical but not for carbanion by breaking away from the concrete condition of these reactions. Of course, in general, a $CH_3^{\bullet}$ free radical is more stable than a $C_6H_5^{\bullet}$ free radical, but the stability of a CH_3^- anion is lower than that of a $C_6H_5^-$ anion. However, these authors made a mistake by oversight that the O—C (aromatic) bond of a phenyl group in Wittig rearrangement and N^+—C (aromatic) bond of a phenyl group in Stevens rearrangement develop a stronger double bond character, but the O—C(aliphatic) and N^+—C (aliphatic) of a alkyl group in corresponding rearrangement possess only single bond character. These differences have been evidenced by bond length and other criterions and would be a well-known common knowledge. Obviously, in these concrete conditions, the formation of the phenyl anion is more difficult than that of alkyl anion due to its additional double bond character. In Grovenstein-Zimmermann rearrangement, the variation of the electron configuration during the reaction is identical to that in Wittig and Stevens rearrangements, however, in this circumstance, the migrating phenyl group links the carbon atom only with a single bond but without the additional π-bond order which is the same as that of a C-alkyl bond. It has been evidenced by experiments that the sequences of migratory aptitude in Grovenstein-Zimmermann rearrangement are C_6H_5— > CH_3—(in eq. (5)) and C_6H_5— > p-$CH_3C_6H_4$—(in eq. (6)). Therefore, the migratory aptitude of an aryl group will be higher than that of an alkyl group if there is no additional double bond character induced by an aryl group to be consistent with its anion stability[14].

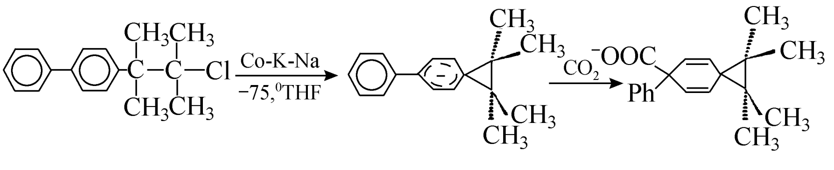


$$(C_6H_5)_2C(CH_3)CH_2^{\ominus}Li^{\oplus} \longrightarrow C_6H_5\overset{Li^{\oplus}}{\overset{\cdot\cdot\ominus}{C}}(CH_3)CH_2C_6H_5 \xrightarrow[(ii)H^+]{(i)CO_2} C_6H_5\underset{COOH}{\underset{|}{C}}(CH_3)CH_2C_6H_5 \qquad (5)$$



$$p\text{-}CH_3C_6H_4\text{-}\underset{CH_3}{\underset{|}{C}}(C_6H_5)CH_3^{\ominus}Li^{\oplus} \longrightarrow \longrightarrow \longrightarrow p\text{-}CH_3C_6H_4\text{-}\underset{COOH}{\underset{|}{C}}(CH_3)CH_2\,C_6H_5 \qquad (6)$$

In a Grovenstein-Zimmermann rearrangement as illustrated in eq. (7), a phenonanion analogous to Meisenheimer salt structure has been detected at a low temperature during the migration of biphenyl group[10]. It is shown that the electron pair in the anion is excited up to NBMO orbit, or in other words, the electron pair carried by biphenyl group is excited up to LUMO orbit at first before the formation of the bridged phenonanion ion. It is also shown that a complex by combining an anion with both π and π^* orbits proposed by us is not only present but also can be separated in certain special case.



(7)

3 Conclusion

Only few 1,2-shifts have been discussed with advanced semi-empirical quantum calculation by the previous authors[12,15]. Systematical treatments on the mechanism of various 1,2-shifts with MNDO or other models in MOPAC, through the large quantity calculation on typic reactions, have been undertaken in recent years in our laboratory. A π-complex transition state mechanism with general significance to all the rearrangements of 1,2-shift has been put forward, and the puzzling characters of 1,2-anion shifts such as Wittig and Steven rearrangements have been explained reasonably with π-complex mechanism. Additionally, the transition state configurations in the Beckmann rearrangement of (E)-acetophenone oxime and in the benzoin rearrangement have been determined with PM3 model. The configuration of the transition complex 2-phenyl-tetrame- thylethyl cation has been calculated by MNDO method. But the configuration in transition state of 2-biphenylyl-tetramethylethyl anion has been predicted through AM1 system because of its better results on the calculation for the conformation of biphenyl. All the calculated configurations of the transition states on the saddle points emerge from a newly formed π-bond skeleton, as in the first case to form an acetylene like linear structure or as in the latter three cases to form an ethylene like coplanar structure, and the migrating benzene ring in all the above-mentioned cases situated near the center of A-B bond takes a configuration, which is perpendicular to both A-B bond and the transition state plane. The present quantum chemical calculations give a result being highly consistent with the experimental facts, and the theoretical treatment by combining with the facts goes beyond the pure experimental investigation, which might uncover a general rule of the reaction mechanism.

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