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The controversial reaction mechanism of Stevens rearrangement: A review

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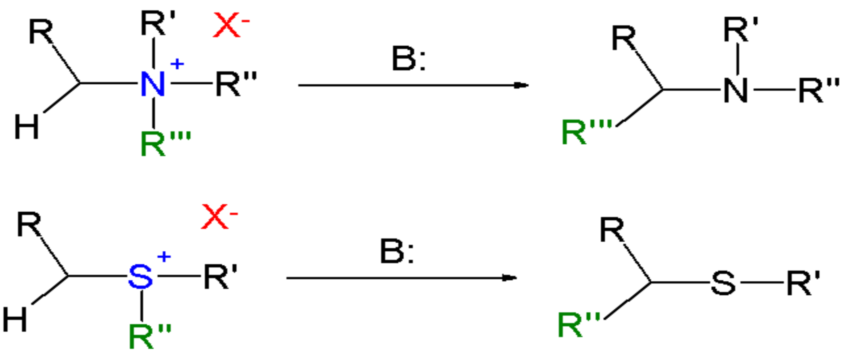
ABSTRACT
From the date of discovery the Stevens Rearrangement is one of the most important name reactions and it is still under investigation due to its controversial reaction mechanism. Though the radical pair mechanism has much more theoretical and CIDNP proof over ionic pair mechanism and other mechanisms in controlling the Stevens rearrangement but still it is in doubt because of its noncompatibility with some abnormal products. This paper goes through all the reaction mechanisms proposed by various scientists on Stevens Rearrangement and their theoretical or chemical explanations.

INTRODUCTION

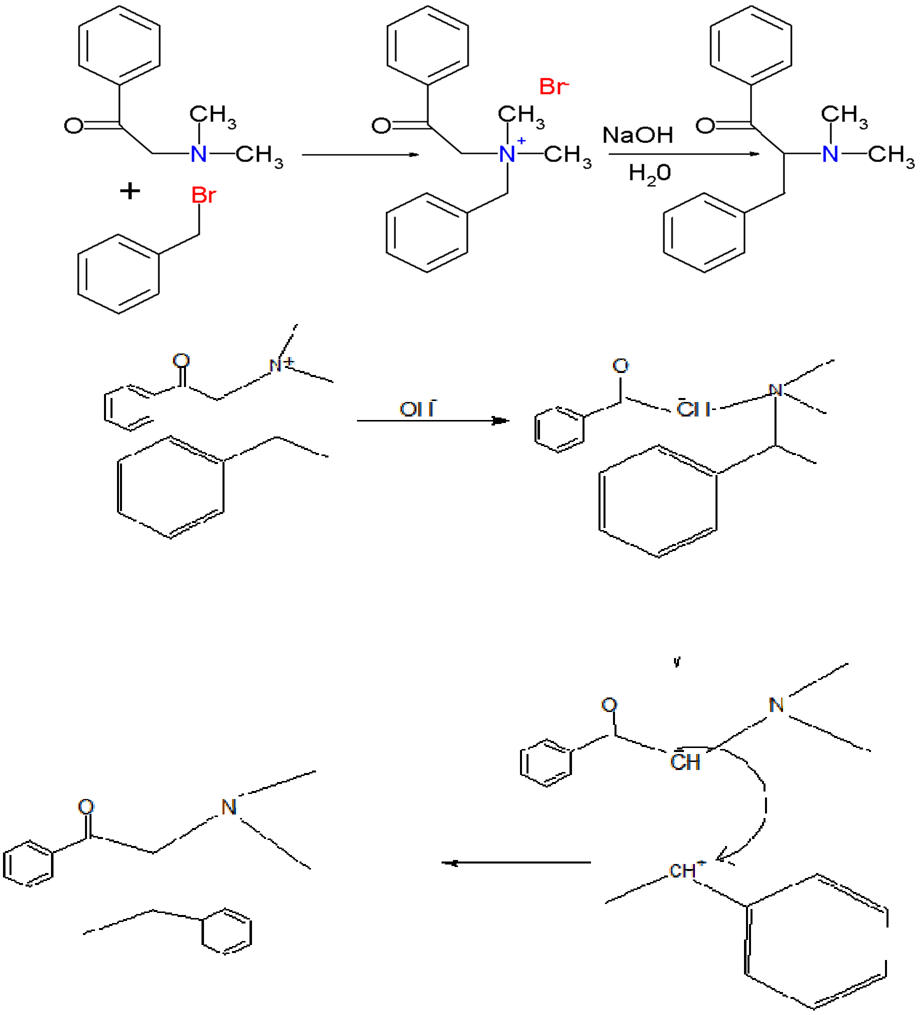
The Stevens rearrangement in organic chemistry is an organic reaction converting quaternary ammonium salts and sulfonium salts to the corresponding amines or sulfides in presence of a strong base in a 1,2-rearrangement[1].



The reactants can be obtained by alkylation of the corresponding amines and sulfides. The substituent **R** next the amine methylene group is an electron-withdrawing group.

Originally the reaction mechanism of the Stevens Rearrangement is proposed by T.S.Stevens. But till to date the reaction mechanism of the Stevens Rearrangement of the ammonium ylides is very much controversial and a topic of much discussion.

The original 1928 publication by T.S. Stevens[2] concerned the reaction of *1-phenyl-2- (N, N-dimethyl) ethanone* with benzyl bromide to the ammonium salt followed by the rearrangement reaction with sodium hydroxide in water to the rearranged amine.



The Ionic Pair Mechanism(Stereochemistry not important)

Figure 1. The Ionic Pair Mechanism

A 1932 publication by T.S.Stevens described the corresponding sulfur reaction[3].

The reaction mechanism of the Stevens Rearrangement as first believes through the "Ionic –Pair mechanism"[4] which is deplicated as below (Figure 1).This mechanism is proposed by Johnstone and Stevens and this is believed to the mechanism if the R is a phenyl group.

This happens because the transition structure is stabilized by delocalization of the partial charge, while this effect is not present in the phenyl radical or anion preventing the two-step mechanisms. The lack of hydrogen atoms bound to the migrating carbon avoids their steric hindrance and also led to a more stable transition structure. Such conditions are found only when the migrating carbon belongs to an aromatic ring.

Hauser and Kantor[5] questioned the validity of this mechanism and proposed an alternative pathway involving an intramolecular nucleophilic substitution S_Ni in which the migrating group departs with its pair of electrons. This also retains the optical activity in the migrating group. This is in defiance of the orbital symmetry rule of Woodward-Hoffmann[6]. Brewster and Klein[7] have supported this mechanism.

The mechanism is illustrated below (Figure 2),

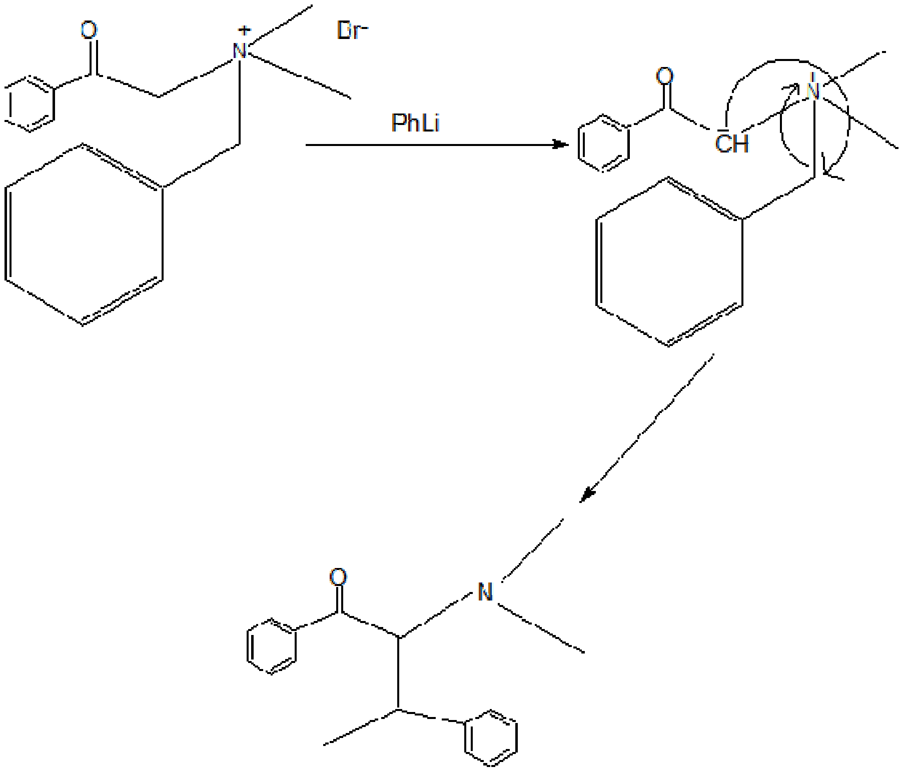


Figure 2. The alternative mechanism proposed by Hauser and Kantor

But it should be noted that even the S_Ni reactions of chlorosulfides don't always proceed with the retention of configuration. A tight ion-pair has been proposed instead as an intermediate in such reactions.

Hill and Chan[8] reported that the alkylbenzylmethyl ammonium cation gave 15 % of the normal product which is optically active (Figure 3). The formation of this product can be explained by invoking either of the above two mechanisms.

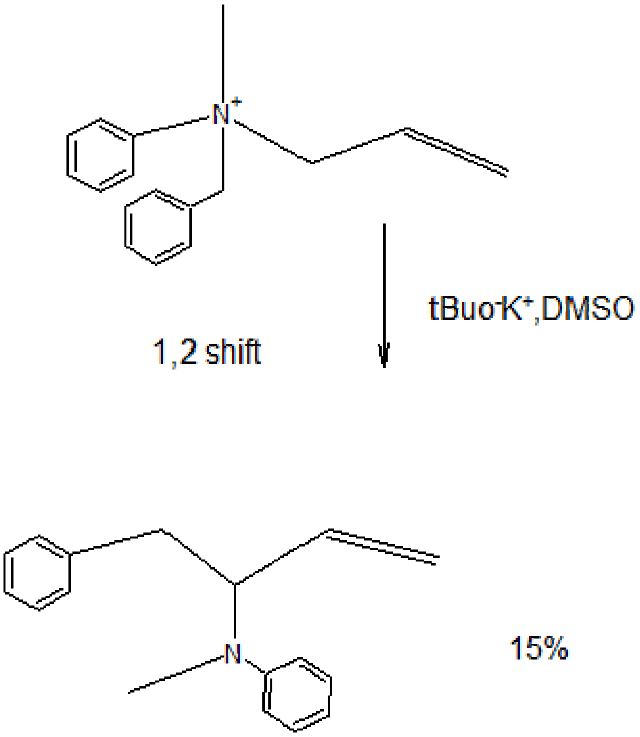


Figure 3. The illustration of Stevens Rearrangement by Hill and Chan

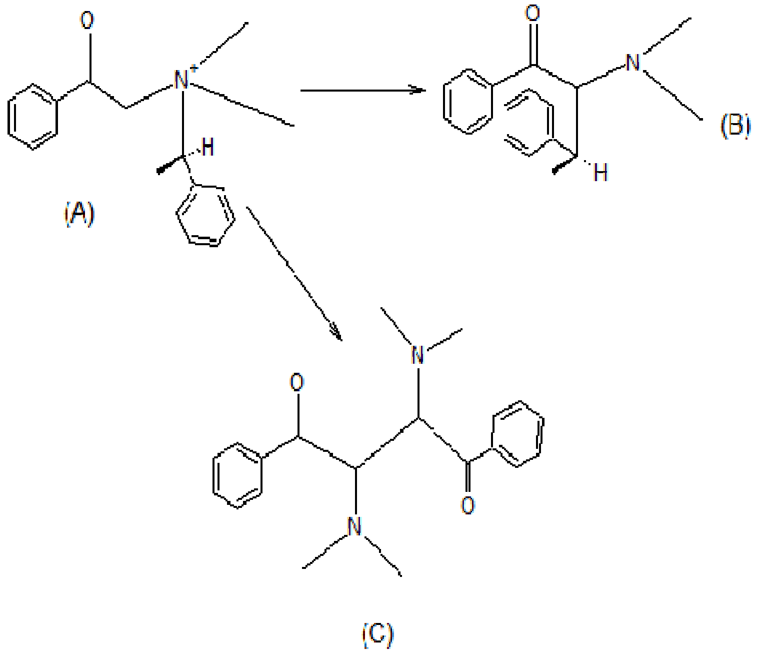


Figure 4. Formation of Normal and Abnormal product in Stevens Rearrangement

Evidence has accumulated[9, 10] for the radical pair mechanism for explanation of Stevens Rearrangement. Analogous to Wittig rearrangement and the observation that the Stevens rearrangement proceeds via partial retention of configuration of the migrating group led to suggest the radical pair mechanism. For instance optically active 3° amine (A) rearranged to (B) {normal product} with only partial retention of stereochemical integrity. Another product (C) {abnormal product} was also isolated[11] (Figure 4).

Chemically Induced Dynamic Nuclear Polarization [12,13]spectra observed in many cases also supported the radical pair mechanism which is deplicated below (Figure 5).

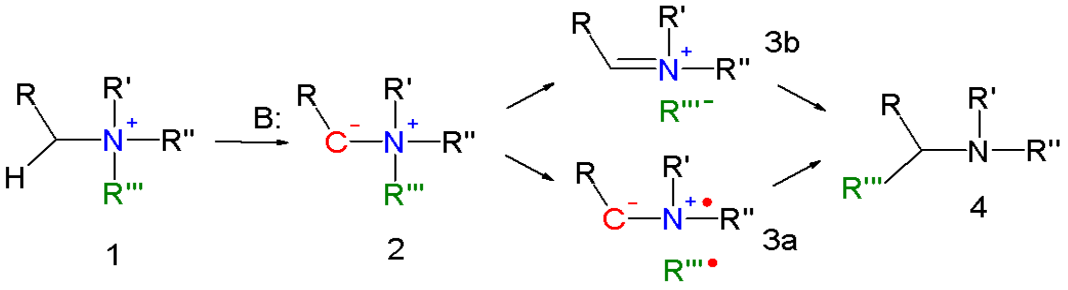


Figure 5. The radical pair mechanism of Stevens Rearrangement

Theoretical Investigation of the Reaction Mechanism

The first theoretical study was performed in 1974 by Dewar et al.[14], who pointed out that the key step of the rearrangement could be a case of breakdown of the Woodward- Hoffmann rules because of the high exothermicity of the reaction. The migration would take thus place through a “formally forbidden” concerted tight transition structure with retention of configuration. The energy barrier, calculated by the semiempirical method MINDO/3, was only 4 kcal mol^{-1} high. However, the energy of the separated radicals was calculated as-10 kcal mol^{-1} with respect to the ylide. Therefore, the authors concluded that it was not possible to distinguish between the two mechanisms (“ionic pair” and “radical pair” mechanisms).Thereafter in 1990s Heard and Yates[15-20] studied the reaction mechanism of the Stevens

Rearrangement extensively via semiempirical (MINDO) and ab initio (HF, MP2, MP4, CCSD) methods. In all cases they concluded that the radical pair mechanism by 20-40 kcal/mol. The optimized geometries by Heard and Yates are also in good agreement, and the ionic pair mechanism was also found to be non-competitive.

But the diradical pathway of the Stevens Rearrangement was not fully investigated by Heard and Yates since they always give reference to the separated radicals.

Recently Ghigo et al.[21] fully investigated the mechanism of the Stevens Rearrangement on several substrates. This study suggests that the reaction takes place by a diradical mechanism through the hemolytic dissociation of the C-N bond in the ylide to form a radical couple. This step follows by radical coupling of either retention of configuration or the inversion of conversion (Figure 6) [TS=Transition state].

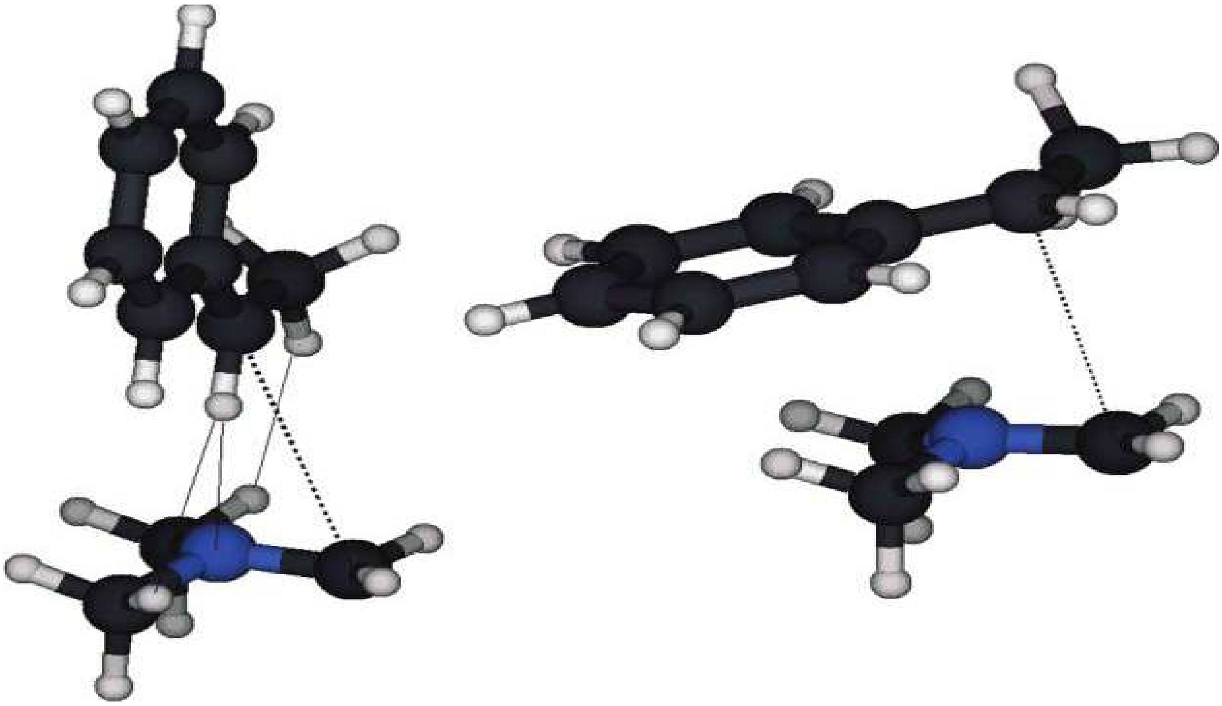


Figure 6. TS radical coupling with configuration inversion (left) and configuration retention (right) in the (1-phenylethyl)-dimethyl ammonium ylide[21]

They also find that there is an exception to the diradical mechanism when the migrating group is phenyl; they observed that in that case the migration takes place via a concerted closed-shell polar transition structure and the mechanism is similar to the ionic pair mechanism.

CONCLUSION

But neither Heard and Yates nor Ghigo et al. explained the formation of the product (C) [11]. This is still in doubt that whether the ionic pair mechanism or the radical pair mechanism which one prefers in the formation of the product (C). Neither of them gives the explanation on the formation of the coupling product R-R[22-25]. Because of these lackings the doubt still continues on the mechanism of a typical Stevens Rearrangement. But still now as per CIDNP study and some theoretical investigations the Radical pair mechanism has an edge over the Ionic pair mechanism in explanation of the reaction mechanism of Stevens Rearrangement.

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