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The mechanism of the *Stevens* and *Sommelet-Hauser* Rearrangements. A Theoretical Study.

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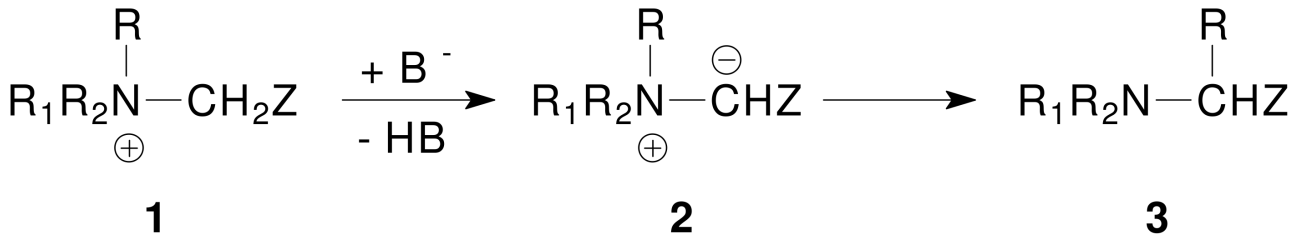
ABSTRACT: The [1,2] and [2,3] migration steps in the *Stevens* and *Sommelet-Hauser* rearrangements which occur in the ylids of quaternary ammonium salts have been studied M05-2x levels. The *Stevens* migration has been found to take place through a diradical pathway in several cases (tetramethylammonium, benzyltrimethylammonium, benzylphenacyldimethylammonium ylids). By contrast, in the phenyltrimethylammonium ylid this reaction takes place through a concerted process. The *Sommelet-Hauser* takes place through a concerted transition structure. The most important factor determining the extent of competition with the *Stevens* rearrangement is the difference in the reaction energies as the formation of the *Sommelet-Hauser* intermediate is significantly less endoergic.

KEYWORDS: DFT Stevens Sommelet-Hauser Rearrangement

Introduction

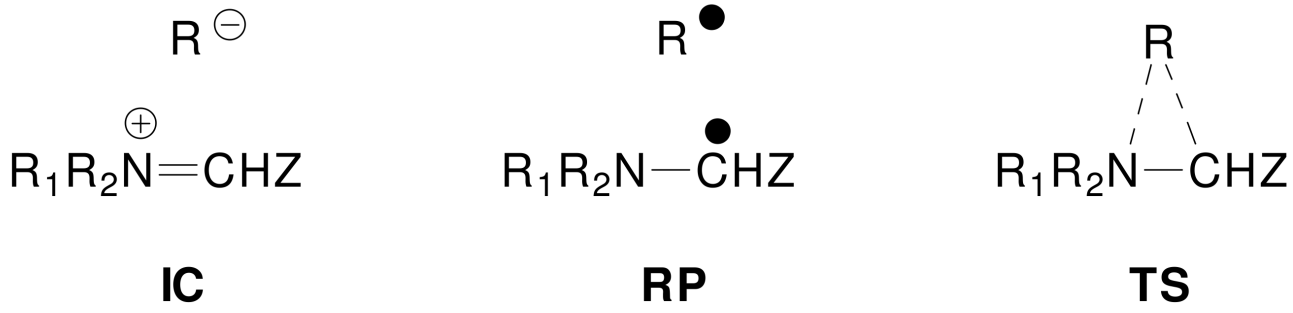
The *Stevens* and *Sommelet-Hauser* rearrangements consist, respectively, in a [1,2] and in a [2,3] migrations that take place in a quaternary ammonium salt when treated with a strong base.[1] The products are tertiary amines. The migrating group can be an alkyl or a benzyl moiety, but, in the former case, only the *Stevens* rearrangements will take place. An electron-withdrawing group Z is often present on one of the carbon atoms bound to the nitrogen. Some interesting cases of the *Stevens* rearrangement involve the migration of aryl[2] or adamantyl groups.[3] The *Stevens* rearrangement presents several synthetic applications[4a] and it has been recently exploited for enantio/diasteroselective synthesis,[4b,c] alkaloid preparations[4d,e] and ring expansion.[4f,g] The *Sommelet-Hauser* rearrangement also presents synthetic applications[5a] for ring expansion[5b] and diasteroselective synthesis.[5c]



Scheme 1 The *Stevens* rearrangemet.

The *Stevens* reaction (Scheme 1)[1b] was first discovered by Thomas S. Stevens *et al.* in 1928 by treating the phenacylbenzyl-dimethylammonium bromide with aqueous sodium hydroxide.[6] It was recognized as an intramolecular migration on the basis of crossover experiments.[7] Later on, 14C labelling confirmed that result.[8] Retention of configuration on the carbon atom of the migrating group bound to the nitrogen atom was also observed.[9] The first step of the reaction was easily identified as the abstraction by the base of the acidic proton on the α-C of the ammonium salt (1) to give an ylid (2), which was then isolated.[10] By contrast, the second step (the [1,2] migration of the R group) has been object of a long discussion.[11] Initially, it was proposed that R migrates as a carbanion[7,12] forming an ion couple (**IC**, Scheme 2) but the observation of the CIDNP effect suggested instead the formation of a radical pair (**RP**, Scheme 2).[13] However, in order not to give R racemization or an alternative radical coupling as that producing R-R (though some exceptions exist[9c,14]), the radicals must combine rapidly.

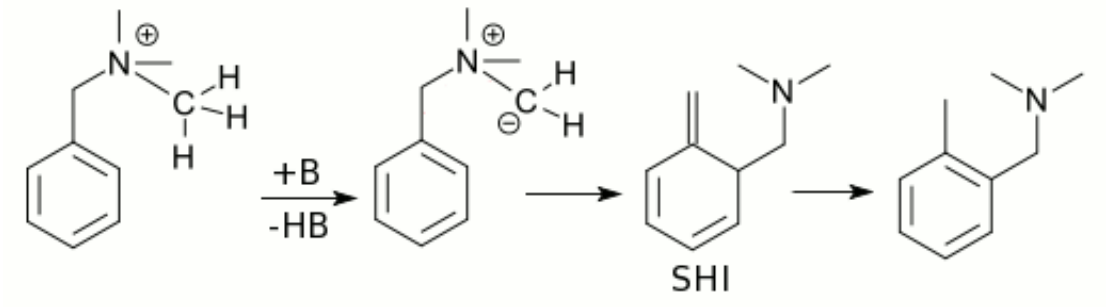
In order to satisfy this condition, the "solvent cage" effect was invoked.[9c,10] The dependence of the reaction stereoselectivity and intramolecularity on temperature and solvent viscosity seems to confirm this explanation.[15] A third mechanism could be a concerted 1,2-shift through a bridged structure (**TS**, Scheme 2) but in this case the orbital symmetry principle would require an inversion of configuration,[16] in disagreement with the experimental findings.



Scheme 2 The proposed mechanisms for the *Stevens* rearrangemet.

The first theoretical study was performed in 1974 by Dewar *et al.*[17] 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 ylid. Therefore, the authors concluded that it was not possible to distinguish between the two mechanisms. Extensive studies by Heard and Yates (H&Y in the forthcoming) followed in the nineties.[18] The authors presented results obtained by several methods, both semiempirical (MNDO) and *ab initio* (HF, MP2, MP4, CCSD). In all cases, the stepwise channel through the radical pair was preferred with respect to the concerted rearrangement by 20-40 kcal mol^{-1}. The latter, however, showed an energy barrier (50-60 kcal mol^{-1}) far higher than Dewar's value, while the geometries were in good agreement. The ion-couple mechanism was also found not competitive. Some recent studies on *Stevens*-like rearrangements also appeared.[19]

The *Sommelet-Hauser* reaction (Scheme 3) consists in a [2,3] sigmatropic rearrangement of type I.[1c,20] It was first observed by Marcel Sommelet in 1937 and studied by Simon C. Kantor and Charles R. Hauser.[21] Its mechanism was quite easily clarified by intermediate isolation[22a,b] (**SHI**, Scheme 3) and labeling experiments.[22c]



Scheme 3 The *Sommelet-Hauser* rearrangement.

When both reactions are possible,[23] the *Stevens* is favored at high temperature, while the *Sommelet-Hauser* is favored at lower temperatures.[23b] There has been little theoretical study on this reaction and a concerted mechanism was found, for the migration of the allyl (mimicking the benzyl group).[18f] This is an expected result because this is permitted by symmetry.

Actually, the diradical pathway in the *Stevens* rearrangement was not fully investigated by H&Y, since they always made reference to the separated radicals. Therefore, in this study the [1,2] migration step will be fully studied including all possible closed shell and diradicaloid species. For suitable substrates the *Sommelet-Hauser* rearrangement will also be considered and, for a selected case, the competition between the two rearrangements will be analyzed.

Theoretical method

Before to proceed with the complete investigation by the density functional method (DFT),[24] some functionals (M05-2x,[25] mPWB1K,[26] and B3LYP[27]) were first tested, comparing, for some representative ylids, *Stevens* products and *Sommelet-Hauser* intermediates, radicals and ions, the energies with those from CBS-QB3.[28] All structures were optimized with the Pople's basis set 6-311+G(d,p)[29a-b] and the

energies refined by single-point calculations with the 6-311+G(3df,2p)[29c] basis set. The mean errors for the three functionals (see Tables S1-S2, Supporting Information) are: -0.3, -3.1, and -9.6 kcal mol^{-1}, respectively. The standard deviations are: 2.2, 3.1, and 6.3 kcal mol^{-1}. The reliability of the M05-2x functional for organic molecules was also observed by other authors.[25c,d] Therefore this functional was used thereafter for the study.

To get a qualitatively correct electronic function and energy estimate relevant to a diradicaloid singlet, as in the radical couple and in some loose transition structures, the spin unrestricted DFT (UDFT) was used. Because this is obtained by allowing the contamination of the restricted singlet electronic function by the triplet (spin contamination) the single-point energy values were then corrected by removing the energy contribution of the triplet electronic function according to an approximate spin projection scheme.[30] The energies of all isolated radicals and closed shell species are not spin projected. Finally, all single points energy values are corrected with the thermal contributions and entropy to the free energy. The nature of the critical points was checked by vibrational analysis.[31] For transition structures (TS), when the inspection of the normal mode related to the imaginary frequency was not sufficient to confidently establish its connection with the initial and final stable species, IRC[32] calculations were performed.

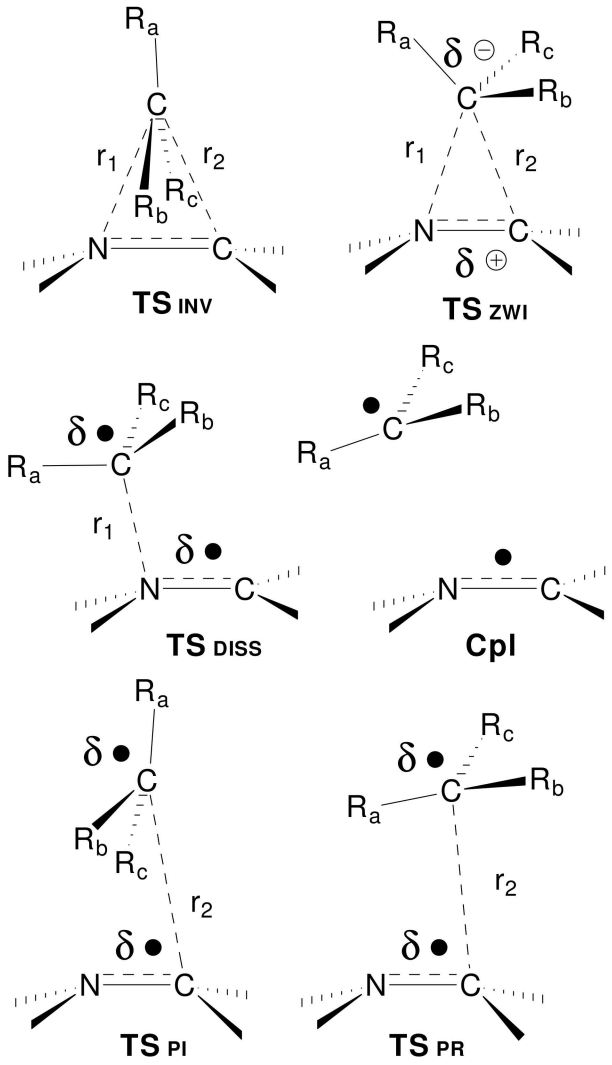
Solvent effects were introduced in the single point energy calculations by the Polarized Continuum Method (IEF-PCM).[33]

All calculations were performed by the quantum package Gaussian 03-E.01.[34]

Figures 1-3 has been obtained with the graphical program molden.[35]

Results and Discussion

The study first focused on the tetramethylammmonium ylid (Schemes 1 and 2: R = R_1 = R_2 = CH_3, Z = H; Table 1) chosen as a prototype of the substrates that undergo the *Stevens* rearrangement. This system had already been studied by Dewar[17] and it was also considered in some of H&Y's papers.[18b-d]



Scheme 4 The relevant structures in the *Stevens* rearrangemet.

The energy value obtained for the two radicals (25 kcal mol^{-1}) can be compared with the semiempirical result by Dewar (-10 kcal mol^{-1})[17] and the best result by B&Y (22 kcal mol^{-1} at the MP4/6-31G(d) level),[18b] both relevant to the separated radicals. The ions generated by the heterolytic bond breaking are located at a very high energy (151 kcal mol^{-1}). The reaction energy (i.e. the relative energy of the amine) is -62 kcal mol^{-1}. This value can be compared with Dewar's (-87 kcal mol^{-1})[17] and the B&Y (-70 kcal mol^{-1}) results.[18b]

The transition structure corresponding to the [1,2] migration with inversion of configuration (**TS$_{INV}$**) was found at 34 kcal mol^{-1}. This structure show some zwitterion character (dipole moment μ = 4.38 D)

ad its relevant geometric parameters (in Å, see Scheme 4, $R_a = R_b = R_c = H$) are $r_1 = 2.532$ and $r_2 = 2.694$.

A zwitterionic transition structure (**TS_{ZWI}**, $\mu = 8.24$ D) for the [1,2] migration with retention of configuration was also found. Its energy (46 kcal mol^{-1}) and geometrical parameters ($r_1 = 2.801$ and $r_2 = 2.783$ Å) can be compared with the structure found by B&Y. In their study the relevant structural parameters were significantly tighter ($r_1 = 1.5$ - 1.8 and $r_2 = 1.9$ - 2.0 Å) and the energy higher (50 - 55 kcal mol^{-1}) but qualitatively similar to our results.

Table 1. M05-2x relative energies (in kcal mol^{-1}) for the *Stevens* rearrangement in the tetramethylammonium ylid in gas phase and solvents.

	$\Delta E^{[a]}$	$\Delta E^{[b]}$	$\Delta G^{[c]}$
Ylid	0.0	0.0	0.0
Radicals	24.0	24.6	6.2
Ions	152.0	151.3	135.3
Amine	-62.6	-61.8	-61.6
TS_{INV}	34.5	34.3	30.6
TS_{ZWI}	46.0	45.5	38.9
TS_{DISS}	23.5	18.7	13.8
Cpl	21.6	20.3	11.1
TS_{PI}	22.1	21.1	11.2
TS_{PR}	22.1	22.6	13.5

[a] Optimized with 6-311+G(d,p). [b] Single point 6-311+G(3df,2p). [c] Free energy values from [b] and thermal contributions.

The radical pathway consists in the homolytic dissociation of the NC bond (**TS_{DISS}**, 19 kcal mol^{-1}, $r_1 = 2.222$, see Scheme 4) to form a radical couple (**Cpl**, 20 kcal mol^{-1}). This is followed by the reassociation of the radicals through two alternative transition structures yielding the *Stevens* product. One would lead to the product with inversion of configuration (**TS_{PI}**, 21 kcal mol^{-1}, $r_2 = 3.460$) the other would lead to a product with retention of configuration (**TS_{PR}**, 23 kcal mol^{-1}, $r_2 = 4.215$).

From the free energies we can deduce that the rate determining step for the [1,2] migration is the homolytic dissociation and that the product should be obtained with configuration inversion. For this model, however, there is no way to experimentally verify this result. Whatever the mechanism, the reaction proceeds through the formation of bound species with a strong diradical character whose complete dissociation to two radicals requires however only 2-3 kcal mol^{-1}.

Table 2. M05-2x relative energies (in kcal mol^{-1}) for the *Stevens* rearrangement in the tetramethylammonium ylid in gas phase and solvents.

	C_6H_{12}[a]	THF[b]	EtOH[c]	DMSO[d]	H_2O[e]
Ylid	0.0	0.0	0.0	0.0	0.0
Radicals	11.9	15.6	15.9	17.3	18.1
Ions	83.7	45.6	35.2	34.3	34.1
Amine	-58.8	-55.8	-54.5	-54.2	-54.0
TS_{INV}	36.2	37.3	37.3	37.8	37.9
TS_{ZWI}	37.2	34.7	33.8	33.9	33.9
TS_{DISS}	17.1	20.3	21.3	21.8	22.1
Cpl	15.4	18.9	19.7	20.5	20.9
TS_{PI}	15.8	19.2	20.0	20.8	21.2
TS_{PR}	18.6	22.3	23.0	24.0	24.2

[a] Cyclohexane, ε=2.0. [b] Tetrahydrofuran, ε=7.6. [c] Ethanol, ε=32.6. [d] Dimethylsufoxide, ε =46.7. [e] Water, ε=78.4

With the introduction of solvent effects (Table 2) we observe that the free energies of the low-polarity radicals (dipole moment μ ≈ 1 Debye), **TS_{DISS}**, (μ = 1.54 D), **Cpl**, (μ = 1.06 D), **TS_{PI}**, (μ = 1.30 D), **TS_{PR}**, (μ = 1.14 D), and product (μ = 0.66 D) are all raised relatively to the more polar ylid (μ = 5.24 D). The relative free energy of the polar **TS_{INV}** is slightly raised by solvents so this pathway is never favored. The separated ions are strongly stabilized in the polar solvents but their relative free energies are at least 10 kcal mol^{-1} above the other species. The **TS_{ZWI}** behaves as a polar species (μ = 8.24 D) and it is only slightly stabilized by the polar solvents with respect to the ylid. Therefore, a ionic

mechanism, either proceeding through a concerted transition structure or full dissociation to ions, is always unfavored.

The study was then extended to the *Stevens* rearrangement on a more realistic substrate: the ylid from neopenthyltrimethylammonium (Schemes 1 and 2: R = $(CH_3)_3CCH_2$, $R_1 = R_2 = CH_3$, Z = H; Scheme 4: $R_a = (CH_3)_3C$, $R_b = R_c = H$).

Both radicals and ions are stabilized by 10 kcal mol^{-1} with respect to the previous case (Table 3). By contrast, the reaction is only slightly more exoergic.

As in the previous case, a polar (μ = 3.97 D) transition structure corresponding to the [1,2] migration with inversion of configuration was found (**TS_{INV}**, 27 kcal mol^{-1}). Due to its high energy it was not considered further.

The diradical pathway was found again to take place through the homolytic dissociation of the ylid (**TS_{DISS}**, 13 kcal mol^{-1}, r_1 = 2.177) to form a radical couple (**Cpl**, 12 kcal mol^{-1}) followed by radical coupling through two alternative transition structures (**TS_{PI}**, 12 kcal mol^{-1}, r_2 = 3.254 and **TS_{PR}**, 17 kcal mol^{-1}, r_2 = 3.800) yielding the amine.

The neopenthyltrimethylammonium ylid was studied by Pine[12] who suggested an ion pair mechanism on the basis of the formation of neopenthane, but in the present study the zwitterionic transition structure was not found. Any attempt to localize it indicates apparently a different process: the transfer of a H^+ from a methyl to the neopenthyl moiety (**TS_H**, 18 kcal mol^{-1}) yielding neopenthane and a new ylid ($CH_3N(CH_2)_2$). Their complex (**Cpl_H**) is found at -20 kcal mol^{-1}. However, the IRC indicates that **TS_H** connects **Cpl_H** with the *Stevens* products (far more stable), and not with the ylid. Despite this result, we cannot exclude that **TS_H** could be reached from the ylid because of the possible existence of a bifurcation not identified by the IRC.[37] However, due to its high free energy it was not considered further.

Table 3. M05-2x relative energies (in kcal mol^{-1}) for the *Stevens* rearrangement in the neopenthyltrimethylammonium ylid.

	$\Delta E^{[a]}$	$\Delta E^{[b]}$	$\Delta G^{[c]}$
Ylid	0.0	0.0	0.0
Radicals	16.3	16.5	-4.5
Ions	143.3	142.4	122.9
Amine	-66.6	-65.9	-67.3
TS_{INV}	27.4	27.0	22.1
TS_{DISS}	17.3	13.2	8.6
Cpl	13.7	12.5	1.7
TS_{PI}	14.3	12.5	1.5
TS_{PR}	16.4	16.6	4.9
TS_{H}	17.3	17.7	11.1
Cpl H	-19.4	-20.8	-29.8
H Products	-16.5	-17.9	-35.6
TS_{RHT}	20.0	15.2	4.5

[a] Optimized with 6-311+G(d,p). [b] Single point 6-311+G(3df,2p). [c] Free energy values from [b] and thermal contributions.

Several attempts to find out an ion couple in the gas phase failed and in some of them, the H^+ transfer took place confirming the hypothesis about the possible connection of the ylid with **TS_H**. By contrast, the introduction of solvent effects (DMSO) already during the optimization[38] allowed to optimize the zwitterionic transition structure **TS_{ZWI}**, which is found, however, 16 kcal mol^{-1} above **TS_{DISS}** in terms of free energy.

The formation of neopenthane can be explained if we consider the radical hydrogen transfer in the radical couple (**TS_{RHT}**, 15 kcal mol^{-1}). This process is alternative to the radical coupling leading to the *Stevens* product and the difference between the two competitive process is reduced to less than 0.5 kcal mol^{-1} in term of free energy.

Solvation effects (Table 4) are similar as in the previous case: the free energies of the radicals, **TS_{DISS}** (μ = 1.46 D), **Cpl** (μ = 1.16 D), **TS_{PI}** (μ = 1.17 D), **TS_{PR}** (μ = 1.55 D), **TS_{RHT}** (μ = 1.30 D), **TS_{H}** (μ = 2.13 D) and product (μ = 0.71 D) are all raised relatively to the ylid (μ = 5.60 D). The separated ions are strongly stabilized in the polar solvents but their relative free energies are at least 10 kcal mol^{-1} higher than the other species.

Table 4. M05-2x relative free energies (in kcal mol^{-1}) for the *Stevens* rearrangement in the neopenthyltrimethylammonium ylid in solvents.

	C_6H_{12}[a]	THF[b]	EtOH[c]	DMSO[d]	H_2O[e]
Ylid	0.0	0.0	0.0	0.0	0.0
Radicals	0.4	4.0	4.2	5.5	6.5
Ions	75.5	39.2	28.6	27.8	27.2
Amine	-63.8	-60.3	-59.2	-58.7	-58.4
TS_{DISS}	12.0	15.2	16.1	16.6	16.9
Cpl	6.3	6.9	10.3	11.2	11.6
TS_{PI}	7.0	10.6	11.1	12.3	12.7
TS_{PR}	9.9	13.3	13.8	14.9	15.4
TS_{H}	13.8	16.8	17.8	18.2	18.5
TS_{RHT}	8.0	11.1	11.9	12.5	12.9

[a] Cyclohexane, ε=2.0. [b] Tetrahydrofuran, ε=7.6. [c] Ethanol, ε=32.6. [d] Dimethylsufoxide, ε =46.7. [e] Water, ε=78.4

Therefore, the *Stevens* rearrangement in the ylid from neopenthyltrimethylammonium is described as a radical pair mechanism, in which the dissociation step is the rate determining step. The possible competition of hydrogen-transfer explains the formation of neopenthane as secondary product.

The *Stevens* rearrangement is the only reaction that can take place when the migrating group is aryl as in the ylid of phenyltrimethylammonium (Schemes 1, 2: R = C_6H_5, R_1 = R_2 = CH_3, Z = H; Table 5). This can be seen as a model for some species object of experimental works where the migrating group were actually tetrafluorophenyl[2a] and 1-naphthyl.[2b]

Table 5. M05-2x relative energies (in kcal mol^{-1}) for the *Stevens* rearrangement in the phenyltrimethylammonium ylid.

	$\Delta E^{[a]}$	$\Delta E^{[b]}$	$\Delta G^{[c]}$
Ylid	0.0	0.0	0.0
Radicals	29.9	30.4	12.6
Ions	132.3	132.6	116.8
Amine	-69.1	-68.2	-68.8
TS_{MIG}	17.7	17.4	16.1
Cpl	27.2	27.6	18.2

[a] Optimized with 6-311+G(d,p). [b] Single point 6-311+G(3df,2p). [c] Free energy values from [b] and thermal contributions.

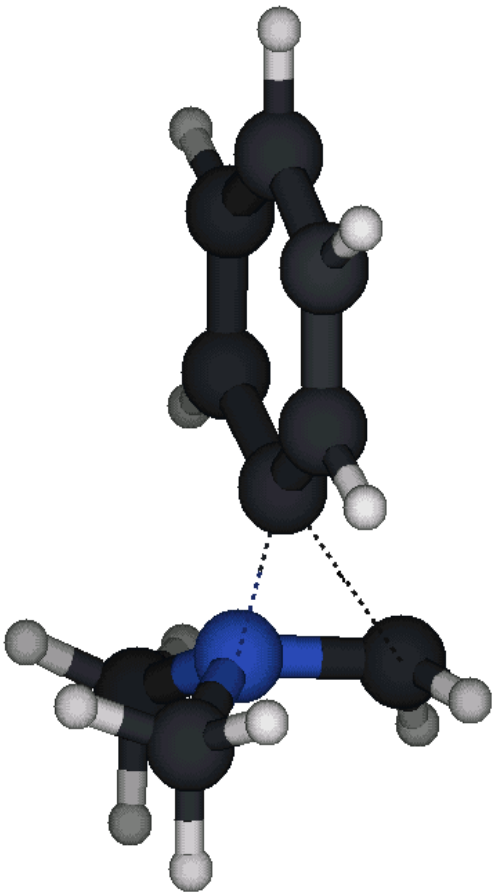


Figure 1 TS *Stevens* migration (TS_{MIG})in the phenyltrimethylammonium ylid.

Differently from all other cases, a concerted transition structure for the [1,2] migration (**TS_{MIG}**, 17 kcal mol^{-1}; Figure 1; r_1 = 1.487 and r_2 = 1.891) was localized. The IRC confirmed that this structure connects the ylid with the amine product without passing through any intermediate.

The low energy of **TS_{MIG}** compared to the free radicals suggested not to fully explore the radical mechanism. Only the radical complex (**Cpl**) was optimized and found 10 kcal mol^{-1} above **TS_{MIG}** confirming the concerted [1,2] migration as the preferred pathway. Inspection of the free energy values does not change this conclusion. If we compare all other cases, we can assume that the free energy of **TS_{DISS}** should be at least 2 kcal mol^{-1} above **Cpl**; this yields a free energy barrier of 20 kcal mol^{-1}.

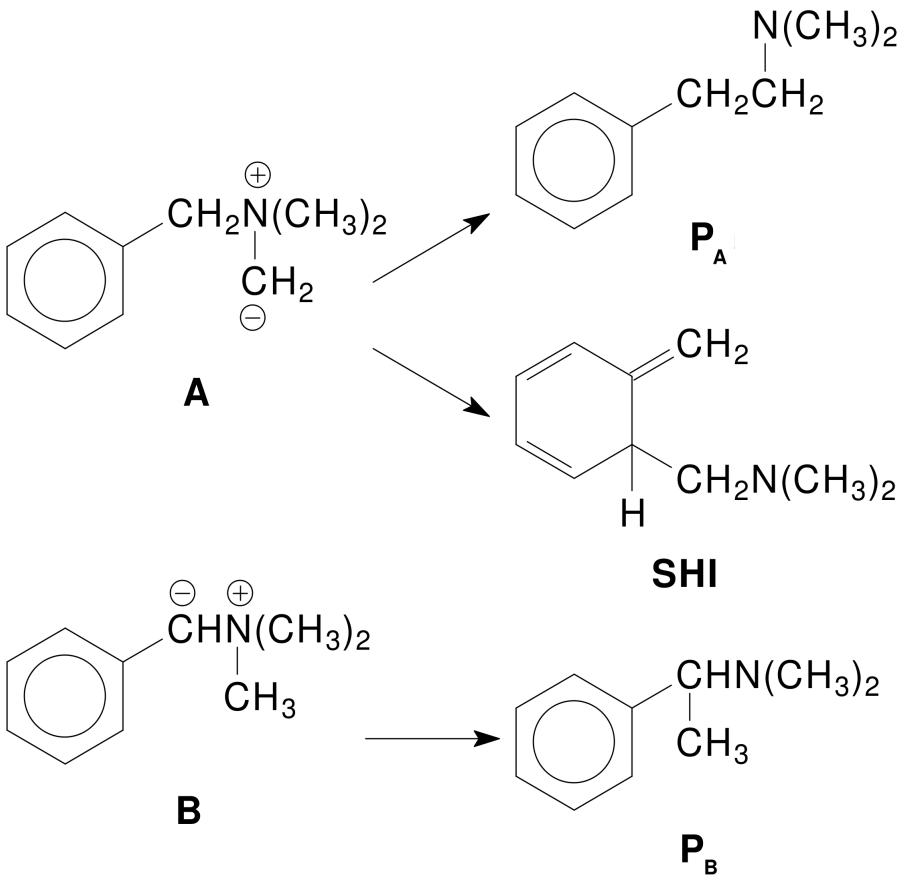
Table 6. M05-2x relative free energies (in kcal mol^{-1}) for the *Stevens* rearrangement in the phenyltrimethylammonium ylid in solvents.

	C_6H_{12}[a]	THF[b]	EtOH[c]	DMSO[d]	H_2O[e]
Ylid	0.0	0.0	0.0	0.0	0.0
Radicals	15.3	17.8	17.9	18.8	19.4
Ions	65.0	25.5	14.3	12.8	11.9
Amine	-66.6	-63.9	-63.0	-62.7	-62.7
TS_{MIG}	16.3	16.8	16.9	16.9	16.8
Cpl	21.6	24.4	24.8	26.7	25.9

[a] Cyclohexane, ε=2.0. [b] Tetrahydrofuran, ε=7.6. [c] Ethanol, ε=32.6. [d] Dimethylsufoxide, ε =46.7. [e] Water, ε=78.4

Solvation effects (Table 6) are similar to previous cases, with radicals and **Cpl** (μ = 1.22 D) are raised in free energy with respect to the ylid (μ = 5.01 D). By contrast, due to its polarity (μ = 5.06 D), the relative free energy of **TS_{MIG}** is basically not sensitive to solvent effects. The relative free energies of the ions are significantly reduced in polar solvents thanks to effective solvation and plummet below the other species in the three more polar solvent. This result suggested to search for an ion couple, but all attempts in the gas phase failed. Therefore, as for the previous case, an optimization was performed in DMSO, where an ion couple was found. This is located 4 kcal mol^{-1} above **TS_{MIG}** both in term of electronic and free energies.[39] Because the formation of the ion couple would require to overcome an energy barrier higher than 4 kcal mol^{-1}, we conclude that the formation of this species, that must precede full dissociation, is unfavored.

In order to observe both the *Stevens* and *Sommelet-Hauser* rearrangements, the study was extended to a model where the *Stevens* migrating group is benzyl, the ylid from benzyltrimethylammonium (Schemes 1, 2: R = C_6H_5-CH_2, R_1 = R_2 = CH_3, Z = H; Scheme 5: **A**). This ylid can be obtained by abstraction of a proton from one of the methyl groups of the benzyltrimethylammonium. Another ylid, more stable, can be obtained by abstraction of a proton from the benzyl group (Scheme 5: **B**) but from this species only the *Stevens* rearrangement is allowed. In most experimental studies on the ylids from the benzyltrimethylammonium only the *Sommelet-Hauser* rearrangement was observed[10b,21,22] while in other both rearrangements were observed.[23a-c] Lepley reported on the role of the base and condition used to prepare the ylid from the ammonium salt,[21b,23b] and put forward the hypothesis that the rearrangements are faster than ylid equilibration.[23c]



Scheme 5 The rearrangements in the benzyltrimethylammonium ylids.

It must be emphasized that in the experiments the *Stevens* product found is $\mathbf{P_B}$ which comes from the ylid **B** while the *Sommelet-Hauser* intermediate **SHI** comes from ylid **A**. Therefore, the latter only

undergoes to *Sommelet-Hauser* rearrangement. The study of the ylid **A** is important also as a model since several experimental studies were performed on systems carrying the benzyl group.[6-9,10a,13,15,23b]

Table 7. M05-2x relative energies (in kcal mol^{-1}) for the *Stevens* and *Sommelet-Hauser* rearrangements in the benzyltrimethylammonium ylid.

	$\Delta E^{[a]}$	$\Delta E^{[b]}$	$\Delta G^{[c]}$
Ylid A	0.0	0.0	0.0
Radicals	10.7	10.8	-8.5
Ions	117.9	116.7	99.0
Amine Pa	-62.2	-61.7	-63.2
S.-H. intermed.	-28.2	-27.7	-30.5
S.-H. product	-64.8	-64.1	-65.1
TS_{INV}	21.6	21.0	16.8
TS_{DISS}	10.5	8.4	5.3
Cpl	6.7	5.3	-3.7
TS_{PI}	8.7	7.8	-1,2
TS_{PR}	7.4	7.7	-0.6
TS_{IC}	23.9	23.5	19.4
IC	20.5	20.0	14.9
TS_{H}	15.6	15.5	9.5
H Products	-9.1	-10.4	-28.4
TS_{SH}	6.9	7.1	5.1
TS_{INT}	14.0	13.1	8.9
Ylid B	-6.0	-6.6	-7.0

[a] Optimized with 6-311+G(d,p). [b] Single point 6-311+G(3df,2p). [c] Free energy values from [b] and thermal contributions.

The study on the ylid **A** (Scheme 5, Table 7) is extended to the *Stevens* and the *Sommelet-Hauser* rearrangements. Delocalization strongly stabilizes both radicals and ions while the *Stevens* rearrangement is only slightly less exoergic than in the previous cases. The formation of the *Sommelet-*

Hauser intermediate (**SHI**, Schemes 3 and 5) is far less exoergic (-28 kcal mol^{-1}). The difference between the two species is very close to the aromatic resonance energy. The energy of the final *Sommelet-Hauser* product, in fact, is close to that one of the *Stevens* product.

The polar transition structure corresponding to the [1,2] migration with inversion of configuration (Scheme 4: $R_a = C_6H_5$, $R_b = R_c = H$; **TS_{INV}**, μ = 3.97 D) was found at 27 kcal mol^{-1}.

The radical mechanism passes again through the homolytic dissociation of the ylid (**TS_{DISS}**, 8 kcal mol^{-1}, r_1 = 2.076) to a diradical complex (**CpI**, 5 kcal mol^{-1}) followed by the two alternative pathways to recombination of the radicals(**TS_{PI}**, 8 kcal mol^{-1}, r_2 = 3.550 and **TS_{PR}**, 8 kcal mol^{-1}, r_2 = 6.075). The complete dissociation to two radicals would requires only 2 kcal mol^{-1}.The zwitterionic migration transition structure was not found. However, a polar structure (**TS_{IC}**, 24 kcal mol^{-1}) leading to an ion couple (**IC**, 20 kcal mol^{-1}) was optimized.

A polar transition structure for the H^+ transfer from a methyl group to the benzyl was found (**TS_H**, 16 kcal mol^{-1}). As in the neopenthyl case, this resulted from the IRC to connect the products (toluene and the ylid $CH_3N(CH_2)_2$) with the *Stevens* product and not with the initial ylid. However, also in this case we cannot exclude that this process could take place from the benzyl ylid as well. At the variance with the neopenthyl case, a radical hydrogen transfer process was not identified in this case.

The transition structure for the formation of the *Sommelet-Hauser* intermediate (**TS_{SH}**, Figure 2, r_{NC} = 1.919 Å, r_{CC} = 3.027 Å) was found at 7 kcal mol^{-1}.

A transition structure (**TS_{INT}**, 13 kcal mol^{-1}) for the interconversion between the *Stevens* product and the *Sommelet-Hauser* intermediate was also localized. However, its role is negligible considering that the effective energy barrier is 75 kcal mol^{-1} starting from the former and 41 kcal mol^{-1} from the latter.

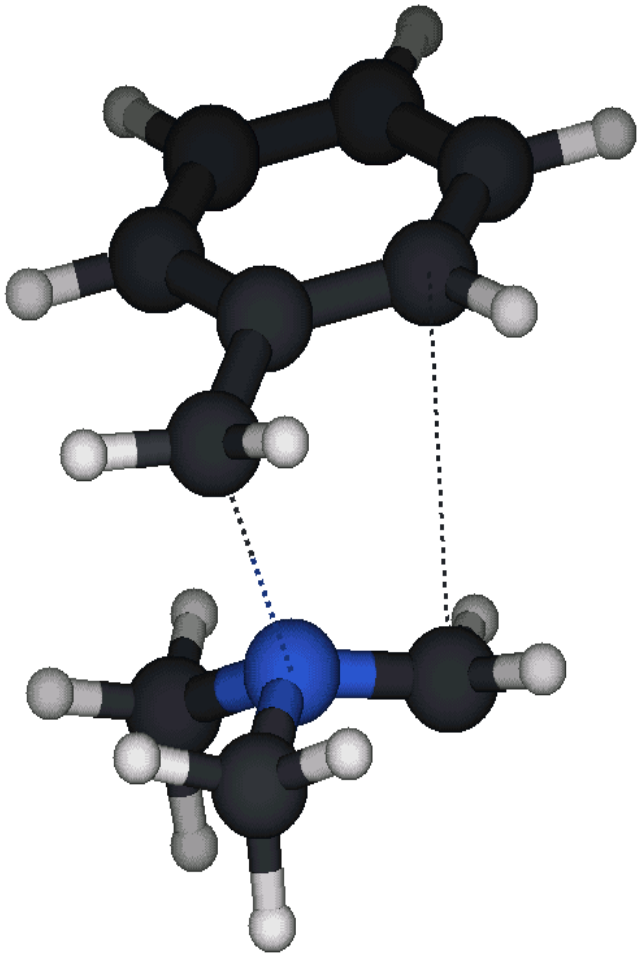


Figure 2 TS *Sommelet-Hauser* migration (TS_{SH}) in the benzyltrimethylammonium ylid.

In terms of free energy, the pathways leading to the *Stevens* product and the *Sommelet-Hauser* intermediate are both favored with respect to the other ones. Both free energy barriers are very low (5 kcal mol^{-1}) and this is in agreement with the hypothesis of Lepley about the slow ylid **A**/**B** interconversion.

As regards the competition between the two rearrangements we can observe that the *Sommelet-Hauser* is always preferred with respect to the *Stevens*, as experimentally found.

Because the activation entropies (3.0 cal mol^{-1} K^{-1} for $\mathbf{TS_{DISS}}$ and 0.3 cal mol^{-1} K^{-1} for $\mathbf{TS_{SH}}$, Table S6, Supporting Information) are different, we can expect a different temperature effect. Table 8 shows the free energy barrier for the two transition structures at 5 different temperatures. The effect is quite

modest but shows a clear trend: a high temperature favours the *Stevens* rearrangement, as experimentally observed.[23d]

Table 8. M05-2x relative free energies (in kcal mol^{-1}) for the *Stevens* and *Sommelet-Hauser* rearrangements in the benzyltrimethylammonium ylid at different temperatures (in °C).

	-33	25	80	120	180
TS_{DISS}	5.4	5.3	5.1	5.0	4.8
TS_{SH}	5.1	5.1	5.1	5.1	5.0

Taking into account solvent effects (Table 9) leads again to an increase in the relative free energies of the radicals, **TS_{DISS}** (μ = 1.39 D), **Cpl** (μ = 0.76 D), **TS_{PI}** (μ = 1.35 D), **TS_{PR}** (μ = 1.20 D), *Stevens* product (μ = 0.72 D) and *Sommelet-Hauser* intermediate (μ = 1.10 D) because of the larger polarity of the ylid (μ = 5.73 D). The ions are strongly stabilized in the polar solvents (ethanol, DMSO and water) and their relative free energies become lower with respect the other species. However, before coming to a complete dissociation, the structure must overcome the barrier (**TS_{IC}**, μ = 8.48 D) for the ion couple formation (**IC**, μ = 8.99 D). This free energy barrier is still 5 - 7 kcal mol^{-1} higher than the other species in these solvents.

Table 9. M05-2x relative free energies (in kcal mol^{-1}) for the *Stevens* and *Sommelet-Hauser* rearrangements in the benzyltrimethylammonium ylid in solvents.

	C_6H_{12}[a]	THF[b]	EtOH[c]	DMSO[d]	H_2O[e]
Ylid A	0.0	0.0	0.0	0.0	0.0
Radicals	-4.6	-1.4	-1.3	-0.2	0.7
Ions	53.0	19.3	9.7	9.0	8.7
Amine P_A	-60.6	-57.7	-57.0	-56.6	-56.2
S.-H. Interm.	-26.9	-23.6	-22.6	-22.1	-21.7
TS_{DISS}	8.2	11.1	12.0	12.4	12.7
Cpl	0.3	3.4	4.2	4.8	5.3
TS_{PI}	3.0	5.9	6.5	7.4	7.9
TS_{PR}	4.0	7.2	8.0	8.8	9.2
TS_{IC}	20.1	18.4	17.4	17.4	17.6
IC	15.2	13.6	12.7	12.7	12.8
TS_H	11.2	13.4	14.2	14.3	14.5
TS_{SH}	7.2	9.3	10.1	10..3	10.5
TS_{INT}	9.1	8.7	8.4	8.5	8.7
Ylid B	-6.7	-6.9	-7.1	-7.0	-6.9

[a] Cyclohexane, ε=2.0. [b] Tetrahydrofuran, ε=7.6. [c] Ethanol, ε=32.6. [d] Dimethylsufoxide, ε =46.7. [e] Water, ε=78.4

In most experimental studies, phenacyl was present as withdrawing group. Therefore, the study was extended to a system bearing this group as well as benzyl as migrating group (Schemes 1 and 2: R = C_6H_5-CH_2, R_1 = R_2 = CH_3, Z = COPh; Scheme 4: R_a = C_6H_5, R_b = R_c = H). This molecule was used in the first experimental studies on the *Stevens* rearrangement[6-8] and was used to demonstrate that the formally forbidden [1,2] migration is preferred with respect to two steps [1,4] and [1,3] migrations involving the carbonyl oxygen.[39] Although this ylid gives both rearrangements, only the *Stevens* has been observed. The main effect of the phenacyl group is to stabilize the carbanion in the ylid, allowing

less severe experimental conditions: sodium alkoxide in alcohols in lieu of sodium amide in liquid ammonia.

As a consequence of ylid stabilization, the relative energy of the two radicals is increased by 18 kcal mol^{-1} with respect to the previous case (Table 10). Due to the presence of the phenacyl group the energy of the ions is increased even more (by 34 kcal mol^{-1}). This suggested to consider the dissociation to ions with inverted charges because of the formation of the stable enolate but the result was discouraging: the energy of these "Inverted Charges" ions is even higher (167 kcal mol^{-1}).

Table 10. M05-2x relative energies (in kcal mol^{-1}) for the *Stevens* and *Sommelet-Hauser* rearrangements in the phenacylbenzyldimethylammonium ylid.

	$\Delta E^{[a]}$	$\Delta E^{[b]}$	$\Delta G^{[c]}$
Ylid	0.0	0.0	0.0
Radicals	29.0	28.5	8.1
Ions	153.5	151.4	130.6
I. C. ions	168.3	167.4	148.8
Amine	-27.3	-26.6	-28.5
S.-H. Interm.	13.1	13.7	11.6
TS_{DISS}	26.9	22.4	17.9
Cpl	23.6	23.3	15.2
TS_{SH}	27.4	27.3	24.4

[a] Optimized with 6-311+G(d,p). [b] Single point 6-311+G(3df,2p). [c] Free energy values from [b] and thermal contributions.

The energies of both the *Stevens* product and the *Sommelet-Hauser* intermediate are also increased. The formation of the latter becomes even endoergic (14 kcal mol^{-1}). This fact and the high energy of the relative transition structure (**TS_{SH}**, 27 kcal mol^{-1}, r_{NC} = 2.561 Å, r_{CC} = 2.212 Å) explain why the [2,3] migration does not take place.

The *Stevens* radical mechanism is favored by 5 kcal mol^{-1} since **TS_{DISS}** it at 18 kcal mol^{-1}. This result is confirmed considering the free energy barriers: **TS_{SH}** is found more than 6 kcal mol^{-1} above **TS_{DISS}**.

The solvent effects (Table 11) are consistent with the previous cases since we observe an increase of the relative free energies of radicals, **TS_{DISS}** (μ = 4.26 D), **Cpl** (μ = 4.28 D), **TS_{SH}** (μ = 3.49 D), *Stevens* products (μ = 2.49 D), and *Sommelet-Hauser* intermediate (μ = 2.84 D) with respect to the more polar ylid (μ = 7.28 D). Obviously, the relative free energies of the ions are reduced too, but they remain significantly higher than the other species even in the more polar solvents.

Table 11. M05-2x relative free energies (in kcal mol^{-1}) for the *Stevens* and *Sommelet-Hauser* rearrangements in the phenacylbenzyldimethylammonium ylid in solvents.

	C_6H_{12}[a]	THF[b]	EtOH[c]	DMSO[d]	H_2O[e]
Ylid	0.0	0.0	0.0	0.0	0.0
Radicals	10.3	12.0	11.6	12.5	13.5
Ions	88.2	56.6	47.6	46.8	46.6
I. C. ions	103.2	68.3	58.0	56.8	56.4
Amine	-24.5	-21.3	-20.2	-19.6	-19.4
S.-H. Interm.	15.3	18.4	19.5	19.8	20.1
TS_{DISS}	20.4	22.4	22.7	23.2	23.7
Cpl	18.7	20.9	21.2	21.8	22.2
TS_{SH}	26.9	29.0	29.9	30.0	30.1

[a] Cyclohexane, ε=2.0. [b] Tetrahydrofuran, ε=7.6. [c] Ethanol, ε=32.6. [d] Dimethylsufoxide, ε =46.7. [e] Water, ε=78.4

The stereochemistry of the Stevens rearrangement has been frequently studied on 1-phenylethyl ylids.[9a,c,15] In most cases a partial retention of configuration on the chiral carbon was observed. Therefore, we extended the study of the radical pathway for the [1,2] migration to a model of such a type of ylid (Schemes 1 and 2: R = C_6H_5-$CH(CH_3)$, R_1 = R_2 = CH_3, Z = H; Scheme 4: R_a = C_6H_5, R_b = H; R_c = CH_3; Table 12).

Table 12. M05-2x relative energies (in kcal mol^{-1}) for the *Stevens* and *Sommelet-Hauser* rearrangements in the (1-phenylethyl)trimethylammonium ylid.

	ΔE[a]	ΔE[b]	ΔG[c]
Ylid	0.0	0.0	0.0
Radicals	7.5	7.4	-12.0
Ions	117.7	116.3	98.5
I. C. ions	177.0	175.8	156.8
Amine	-64.0	-63.5	-64.2
S.-H. Interm.	-30.3	-30.0	-32.2
TS_{DISS}	5.9	6.0	4.6
Cpl	2.1	-0.1	-8.4
TS_{PI}	4.9	4.5	-4.1
TS_{PR}	2.7	2.2	-5.1
TS_{SH}	2.4	2.5	-1.9

[a] Optimized with 6-311+G(d,p). [b] Single point 6-311+G(3df,2p). [c] Free energy values from [b] and thermal contributions.

As in the previous cases, the homolytic dissociation of the CN bond (**TS_{DISS}**, 6 kcal mol^{-1}, r_1 = 2.013) to form the radical complex (**Cpl**, ~0 kcal mol^{-1}) is the rate determining step. Then, this step is followed by the two alternative pathways to recombination of the radicals (**TS_{PI}**, 5 kcal mol^{-1}, r_2 = 3.692 and **TS_{PR}**, 2 kcal mol^{-1}, r_2 = 3.558). The important difference with respect to the other cases, is that the recombination path leading to retention of configuration (**TS_{PR}**) is preferred by 2 kcal mol^{-1}. This result is qualitatively in according with the experimental studies. The higher energy of **TS_{PI}** is probably due to the steric hindrance of the methyl group which is pointing towards the NC bond (Figure 3). This effect is not present (or sensibly reduced) in **TS_{PR}**.

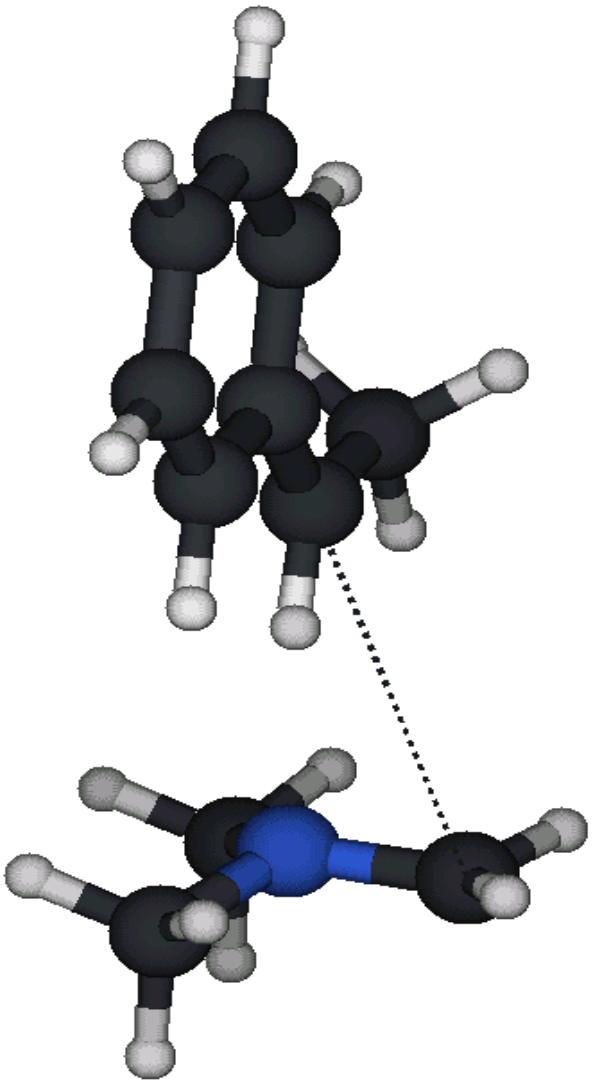


Figure 3. TS radical coupling with configuration inversion (TS_{PI}) in the (1-phenylethyl)dimethylammonium ylid

The solvent effects (Table 13) do not change with respect to previous cases: we observe an increase of the relative free energies of radicals, **TS_{DISS}** (p = 1.13 D), **Cpl** (p = 0.49 D), **TS_{PI}** (p = 1.57 D), **TS_{PR}** (p = 0.69 D), and *Stevens* products (p = 0.71 D) with respect to the more polar ylid (p = 5.37 D). The free energy difference between **TS_{PI}** and **TS_{PR}** is always 2 kcal mol^{-1}. This substantial not dependence of this free energy difference from the solvent polarity is in agreement of the latest experimental evidences where the stereoselectivity of the *Stevens* rearrangement has been found to depend on the viscosity of the solvent (and on the temperature through this parameter) and not the polarity.[15]

Table 13. M05-2x relative free energies (in kcal mol^{-1}) for the *Stevens* and *Sommelet-Hauser* rearrangements in the (1-phenylethyl)trimethylammonium ylid in solvents.

	C_6H_{12}[a]	THF[b]	EtOH[c]	DMSO[d]	H_2O[e]
Ylid	0.0	0.0	0.0	0.0	0.0
Radicals	-8.5	-5.5	-5.5	-4.3	-3.4
Amine	-61.3	-58.3	-57.5	-57.0	-56.9
TS_{DISS}	6.9	9.4	10.3	10.5	10.7
Cpl	-5.0	-2.0	-1.2	-0.7	-0.4
TS_{PI}	0.2	3.3	3.8	4.8	5.1
TS_{PR}	-1.7	1.3	2.3	2.7	3.1

[a] Cyclohexane, ε=2.0. [b] Tetrahydrofuran, ε=7.6. [c] Ethanol, ε=32.6. [d] Dimethylsufoxide, ε =46.7. [e] Water, ε=78.4

Conclusion

The mechanism of the *Stevens* [1,2] migration has been extensively explored on several substrates. The study suggests that the reaction takes place by a diradical mechanism, through the homolytic dissociation of the CN bond in the ylid (**TS_{DISS}**) to form a radical couple (**Cpl**). This step is followed by the radical coupling that can take place through two alternative pathways: one leading to inversion of configuration (**TS_{PI}**) and the other one to retention of configuration (**TS_{PR}**). Steric considerations suggest that the latter can be slightly preferred in same cases as experimentally observed. These species are held together by a small binding energy (1-6 kcal mol^{-1}, depending on the substrate). Therefore, dissociation to a couple of radicals, often favored in term of free energy, cannot be excluded. So, the "*solvent cage*" effect might play an auxiliary and variable role.

There is an exception to the diradical radical mechanism, when the migrating group is a phenyl: in that case the [1,2] migration takes place through a concerted closed shell transition structure (**TS_{MIG}**).

The heterolytic pathway, let it pass through a concerted zwitterionic transition structure (**TS_{ZWI}**) or through an ion couple (**IC**), is never competitive. The experimental evidence supporting this

mechanism was based on the observation of H^+ transfer products. However, we can explain the formation of these product as the outcome of a secondary reaction pathway which flanks the radical pathway.

The *Sommelet-Hauser* rearrangement takes place through a concerted transition structure (**TS_{SH}**). The most important factor determining the extent of competition with the *Stevens* rearrangement is the difference in the reaction energies as the formation of the intermediate (**SHI**) for the former is significantly less endoergic (35 kcal mol^{-1}). Therefore, for very stable ylids (e.g. when a Z group is present), the *Stevens* rearrangement becomes the preferred reaction. When both rearrangements are exoergic, the temperature may have a role, since the *Sommelet-Hauser* rearrangement is favored at lower temperatures and the *Stevens* rearrangement at higher temperatures, because of the different entropy in the two rate determining steps.

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Supporting Information Available. Tabulated energies and Cartesian coordinates from DFT calculations. This material is available free of charge via the World Wide Web at http://pubs.acs.org.

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	Δ*E*(a)	Δ*E*(b)	Δ*G*(c)
TS_{DISS}	24.4	19.5	15.2
TS_{ZWI}	38.7	37.8	31.4

(39) Tests on the ylid from the phenyltrimethylammmonium. M05-2x + PCM(DMSO) energy values (kcal mol-1): (a) 6-311+G(d,p); (b) single point 6-311+G(3df,2p); (c) free energy.

	Δ*E*(a)	Δ*E*(b)	Δ*G*(b)
TS_{MIG}	19.0	18.6	16.8
Ion Couple	22.7	23.0	20.8

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SYNOPSIS TOC