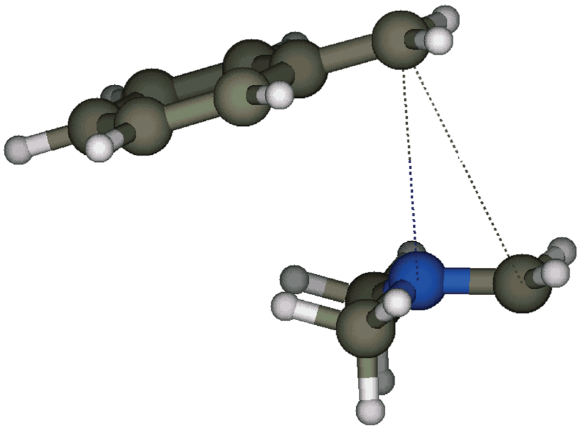
JOC Article
pubs.acs.org/joc

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

Giovanni Ghigo,* Stefania Cagnina, Andrea Maranzana, and Glauco Tonachini
Dipartimento di Chimica Generale e Chimica Organica, C. so M. d'Azeglio 48, I-10125 Torino, Italy

giovanni.ghigo@unito.it

Received March 1, 2010



The [1,2] and [2,3] migration steps in the Stevens and Sommelet−Hauser rearrangements which occur in the ylides of quaternary ammonium salts have been studied at M05-2x levels. The Stevens migration has been found to take place through a diradical pathway in several cases (tetramethylammonium, benzyltrimethylammonium, benzylphenacyldimethylammonium ylides). By contrast, in the phenyltrimethylammonium ylide this reaction takes place through a concerted process. The Sommelet−Hauser rearrangement 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.

Introduction

The Stevens and Sommelet−Hauser rearrangements consist, respectively, of [1,2] and [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]

---

[1] (a) Sweene, J. B. *Chem. Soc. Rev.* **2009**, *38*, 1027–1038. (b) March, J. *March's Advanced Organic Chemistry*; John Wiley & Sons, Inc.: New York, 2001; Chapters 18−21, pp 1419−1421. (c) Reference 1b, Chapter 3-27, pp 605−606.

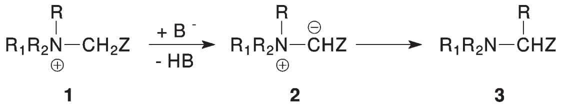
[2] (a) Heaney, H.; Ward, T. J. *Chem. Commun.* **1969**, 810. (b) Truce, W. E.; Heuring, D. L *Chem. Commun.* **1969**, 1499–1500.

[3] (a) Adams, B. L.; Liu, J.-H.; Kovacic, P. *Tetrahedron Lett.* **1974**, *5*, 427–428. (b) Frey, J. L.; Adlington, M. G.; Badger, R. C.; McCullough, S. K. *Tetrahedron Lett.* **1974**, *5*, 429–432.

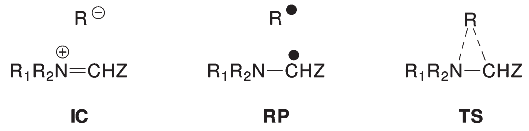
[4] (a) Marko, I. E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 3, pp 913−927. (b) Gonçalves-Farbos, M.-H.; Vial, L.; Lacour, J. *Chem. Commun.* **2008**, 829–831. (c) Tayama, E.; Orihara, K.; Kimura, H. *Org. Biomol. Chem.* **2008**, *6*, 3673–3680. (d) González-Gómeza, Á.; Domíngueza, G.; Amadora, U.; Pérez-Castells, J. *Tetrahedron Lett.* **2008**, *49*, 5467–5470. (e) Vanecko, J. A.; Wan, H.; West, F. G. *Tetrahedron* **2006**, *62*, 1043–1062. (f) Ellis-Holder, K. K.; Peppers, B. P.; Kovalevsky, A. Y.; Diver, S. T. *Org. Lett.* **2006**, *12*, 2511–2514. (g) Gawley, R. E.; Moon, K. *Org. Lett.* **2007**, *16*, 3093–3096.

DOI: 10.1021/jo100367z

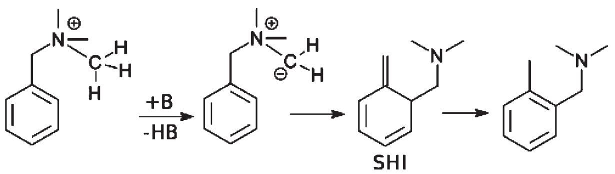
SCHEME 1. **Stevens Rearrangement**



SCHEME 2. **Proposed Mechanisms for the Stevens Rearrangement**



SCHEME 3. **Sommelet−Hauser Rearrangement**



The Stevens reaction (Scheme 1)[1b] was first discovered by Stevens et al. in 1928 by treating the phenacylbenzyldimethylammonium bromide with aqueous sodium hydroxide.[6] It was recognized as an intramolecular migration on the basis of crossover experiments.[7] Later on, ^{14}C labeling 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 ylide (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.

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 ylide. Therefore, the authors concluded that it was not possible to distinguish between the two mechanisms. Extensive studies by Heard and Yates (abbreviated H&Y) followed in the 1990s.[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 to be noncompetitive. Some recent studies on Stevens-like rearrangements also appeared.[19]

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

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.

---

(5) (a) Marko, I. E. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.;Pergamon: Oxford, 1991; Vol. 3, pp 965−971. (b) Popowyez, F.; Mérour, J.-Y.; Joseph, B. *Tetrahedron* **2007**, *63*, 8689–8707. (c) Tayama, E.; Kimura, H. *Angew. Chem., Int. Ed.* **2007**, *46*, 8869–8871.

(6) Stevens, T. S.; Creighton, E. M.; Gordone, A. B.; MacNicol, M. *J. Chem. Soc.* **1928**, 3193–3197.

(7) Stevens, T. S. *J. Chem. Soc.* **1930**, 2107–2113.

(8) Johnstone, R. A. W.; Stevens, T. S. *J. Chem. Soc.* **1955**, 4487–4488.

(9) (a) Brewster, J. H.; Kline, M. W. *J. Am. Chem. Soc.* **1952**, *74*, 5179–5181. (b) Hill, R. K.; Chan, T.-H. *J. Chem. Soc.* **1966**, *88*, 866–867. (c) Schöllkopf, U.; Ludwig, U.; Ostermann, G.; Patsch, M. *Tetrahedron Lett.* **1969**, *39*, 3415–3418.

(10) (a) Jemison, R. W.; Mageswaran, S.; Ollis, W. D.; Potter, S. E.; Pretty, A. J.; Sutherland, I. O.; Thebtaranonth, J. *Chem. Commun.* **1970**, 1201–1202. (b) Puterbaugh, W. H.; Hauser, C. R. *J. Am. Chem. Soc.* **1964**, *86*, 1105–1107.

(11) Pine, S. H. *J. Chem. Educ.* **1971**, 99–102.

(12) Pine, S. H.; Catto, B. A.; Yamagishi, F. G. *J. Org. Chem.* **1970**, *35*, 3663–3665.

(13) (a) Jemison, R. W.; Morris, D. G. *Chem. Commun.* **1969**, 1226–1227. (b) Lepley, A. R. *Chem. Commun.* **1969**, 1460–1462. (c) Lepley, A. R.; Becker, R. H.; Giumanini, A. G. *J. Org. Chem.* **1971**, *36*, 1222–1227. (d) Lepley, A. R. *J. Am. Chem. Soc.* **1969**, *91*, 1237–1239.

(14) Hennion, G. F.; Shoemaker, M. J. *J. Am. Chem. Soc.* **1970**, *92*, 1769–1770.

(15) (a) Ollis, W. D.; Rey, M.; Sutherland, I. O. *J. Chem Soc., Perkin Trans. 1* **1983**, 1009–1027. (b) Chantrapromma, K.; Ollis, W. D.; Sutherland, I. O. *J. Chem Soc., Perkin Trans. 1* **1983**, 1049–11061.

(16) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*: Academic Press: New York, 1970; p 131.

(17) Dewar, M. J. S.; Ramsden, C. A. *J. Chem Soc., Perkin Trans. 1* **1974**, 1839–1844.

(18) (a) Heard, G. L.; Frankcombe, K. E.; Yates, B. F. *Aust. J. Chem.* **1993**, *46*, 1375–1388. (b) Heard, G. L.; Yates, B. F. *Aust. J. Chem.* **1994**, *47*, 1685–1694. (c) Heard, G. L.; Yates, B. F. *THEOCHEM* **1994**, *116*, 197–204. (d) Heard, G. L.; Yates, B. F. *Aust. J. Chem.* **1995**, *48*, 1413–1423. (e) Heard, G. L.; Yates, B. F. *J. Comput. Chem.* **1996**, *17*, 1444–1452. (f) Heard, G. L.; Yates, B. F. *J. Org. Chem.* **1996**, *61*, 7276–7284.

(19) Kakita, K.; Koketsu, J.; Ando, F.; Ninomiya, Y.; Koga, N. *J. Am. Chem. Soc.* **1998**, *120*, 5764–5770.

(20) Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 563–640.

(21) (a) Sommelet, M. *Compt. Rend.* **1937**, *205*, 56. (b) Kantor, S. W.; Hauser, C. R. *J. Am. Chem. Soc.* **1951**, *73*, 4122–4131.

(22) (a) Hauser, C. R.; Van Eenam, D. N. *J. Am. Chem. Soc.* **1957**, *79*, 5512–5530. (b) Pine, S. H.; Sanchez, B. L. *Tetrahedron Lett.* **1969**, *10*, 1319–1320. (c) Jones, F.; Hauser, C. R. *J. Org. Chem.* **1961**, *26*, 2979–2981.

(23) (a) Wittig, G.; Mangold, R.; Fellstschin, G. *Liebigs. Ann.* **1948**, *560*, 116–127. (b) Lepley, A. R.; Becker, R. B. *Tetrahedron* **1965**, *21*, 2365–2373. (c) Lepley, A. R.; Becker, R. B. *J. Org. Chem.* **1965**, *30*, 3888–3891. (d) Wittig, G.; Streib, H. *Liebigs Ann. Chem.* **1953**, *584*, 1–10.

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. In details, the migration will be first studied on the tetramethylammmonium ylide as a prototype of the substrates that undergo this rearrangement. Then the study will be extended to the neopentyltrimethylammonium ylide whose experimental study suggested the ion-couple mechanism[12] and to the phenyltrimethylammmonium ylide as a model of the aromatic systems also the object of experimental studies.[2] For suitable substrates, the Sommelet−Hauser rearrangement will also be considered along with the Stevens rearrangement. In particular, the study will be first focused on the benzyltrimethylammonium ylide. The effects of temperature, the electron-withdrawing group Z, and substitution to the migrating carbon atom will also be the subject of study and compared with the experimental findings. The competition between the Sommelet−Hauser and the Stevens rearrangements and the stereochemistry of the latter will be discussed.

Theoretical Methods

Before proceeding 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 ylides, Stevens products and Sommelet−Hauser intermediates, radicals, and ions, the energies with those from CBS-QB3.[28] All structures were optimized with 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] Therefore this functional was used thereafter for the study.

The DFT method for singlet species provides closed-shell molecules. This prevents a correct study of reaction mechanisms when diradical species and radical couples are involved. Therefore, 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. This is obtained by allowing the contamination of the restricted singlet electronic function by the triplet (spin contamination).[30] The expectation value of the spin operator S^2 applied to the contaminated singlet indicates the diradical character.[30g] All values are reported in the Supporting Information. 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. The energies of all isolated radicals and closed shell species are not spin projected. These single points energy values are first discussed then all values are corrected with the thermal contributions and entropy to the free energy which are also discussed. 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. Finally, solvent effects were introduced in the single point energy calculations by the polarized continuum method (IEF-PCM)[33] and discussed.

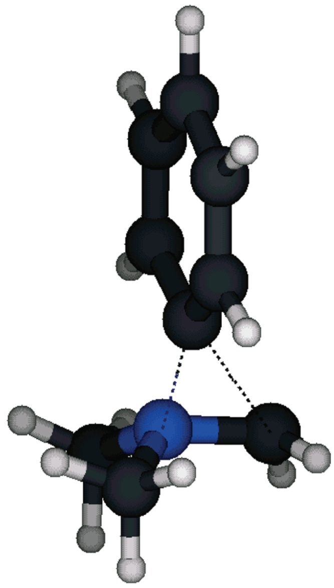


FIGURE 1. TS Stevens migration (TS$_{MIG}$)in the phenyltrimethylammonium ylide.

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 ylide (Schemes 1 and 2: $R = R_1 = R_2 = CH_3$, $Z = H$; Table 1)

---

(24) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989; Chapter 3.

(25) (a) Zhao, Y.; Schultz, N. E.; Truhlar, D. G. *J. Chem. Theory Comput.* **2006**, *2*, 364–382. (b) Zhao, Y.; Truhlar, D. G. *Org. Lett.* **2006**, *8*, 5753–5755. (c) Wodrich, M. D. W.; Corminboeuf, C.; Schreiner, P. R.; Fokin, A. A.; Schleyer, P. v. R. *Org. Lett.* **2007**, *9*, 1851–1854.

(26) (a) Adamo, C; Barone, V. *J. Chem. Phys.* **1998**, *108*, 664–675. (b) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2004**, *108*, 6908–6918. (c) Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157–167.

(27) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.

(28) (a) Montgomery, J. A., Jr; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **1999**, *110*, 2822–2827. (b) Montgomery, J. A.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A *J. Chem. Phys.* **2000**, *112*, 6532–6542.

(29) (a) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639–5348. (b) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294–301. (c) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265–3269.

(30) (a) Isobe, H.; Takano, Y.; Kitagawa, Y.; Kawakami, T.; Yamanaka, S.; Yamagichi, K.; Houk, K. N. *J. Phys. Chem. A* **2003**, *107*, 682–694. (b) Goldstein, E.; Beno, B.; Houk, K. N. *J. Am. Chem. Soc.* **1995**, *118*, 6036–6043. (c) Yamanaka, S.; Kawakami, T.; Nagao, K.; Yamaguchi, K. *Chem. Phys. Lett.* **1994**, *231*, 25–33. (d) Yamaguchi, K.; Jensen, F.; Dorigo, A.; Houk, K. N. *Chem. Phys. Lett.* **1988**, *149*, 537–542. (e) Cramer, C. J.; Dulles, F. J.; Giesen, G. J.; Almlöf, J. *Chem. Phys. Lett.* **1995**, *245*, 165–170. (f) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257–2261. (g) Bally, T.; Borden, W. T. In *Reviews in Computational Chemistry*; Lipowitz, K. B., Boyd, D. B., Eds.; Wiley: New York, 1999. (h) Wittbrodt, J. M.; Schlegel, H. B. *J. Chem. Phys.* **1996**, *105*, 6574–6577. (i) Kitagawa, Y.; Saito, T.; Nakanishi, Y.; Kataoka, Y.; Matsui, T.; Kawakami, T.; Okumura, M.; Yamagichi, K. *J. Phys. Chem. A* **2009**, *1113*, 15041–15046.

(31) Reaction free energies were computed as outlined, for instance, in: (a) Foresman, J. B.; Frisch, ó. *Exploring Chemistry with Electronic Structure Methods*; Gaussian, Inc.: Pittsburgh, 1996; pp 166−168. (b) McQuarrie, D. A. *Statistical Thermodynamics*; Harper and Row: New York, 1973.

(32) (a) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154–2161. (b) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523–5527. and references cited therein.

(33) (a) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995–2001. (b) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. *J. Chem. Phys.* **2001**, *114*, 5691–5701. (c) Cancès, M. T.; Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3032–3041. (d) Cossi, M.; Barone, V.; Mennucci, B.; Tomasi, J. *Chem. Phys. Lett.* **1998**, *286*, 253–260. (e) Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *106*, 5151–5158.

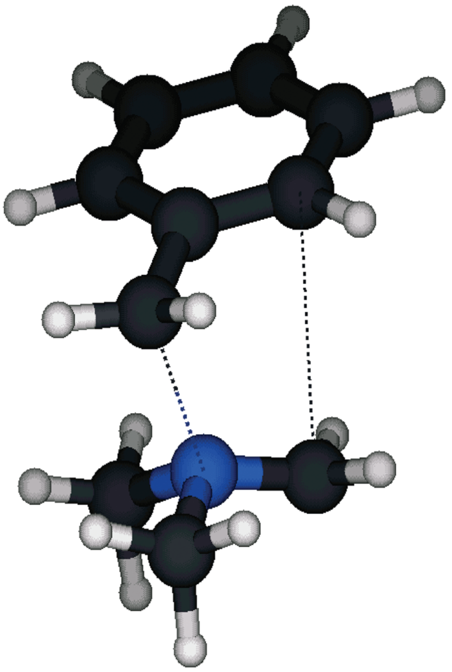


FIGURE 2. TS Sommelet−Hauser migration ($\mathrm{TS}_{\mathrm{SH}}$) in the benzyltrimethylammonium ylide.

TABLE 1. M05-2x Relative Energies (in kcal mol^{-1}) for the Stevens Rearrangement in the Tetramethylammonium Ylide in the Gas Phase

	ΔE^{a}	ΔE^{b}	ΔG^{c}
ylide	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
$\mathrm{TS}_{\mathrm{INV}}$	34.5	34.3	30.6
$\mathrm{TS}_{\mathrm{ZWI}}$	46.0	45.5	38.9
$\mathrm{TS}_{\mathrm{DISS}}$	23.5	18.7	13.8
Cpl	21.6	20.3	11.1
$\mathrm{TS}_{\mathrm{PI}}$	22.1	21.1	11.2
$\mathrm{TS}_{\mathrm{PR}}$	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.

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]

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 H&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 H&Y (−70 kcal mol^{-1}) results.[18b]

The transition structure corresponding to the [1,2] migration with inversion of configuration (**$\mathrm{TS}_{\mathrm{INV}}$**) was found at 34 kcal mol^{-1}. This structure shows some zwitterion character (dipole moment $\mu = 4.38$ D), and its relevant geometric parameters (in Å, see Scheme 4, $\mathrm{R_a} = \mathrm{R_b} = \mathrm{R_c} = \mathrm{H}$) are $r_1 = 2.532$ and $r_2 = 2.694$.

A zwitterionic transition structure (**$\mathrm{TS}_{\mathrm{ZWI}}$**, $\mu = 8.24$ 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 H&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.

The radical pathway consists in the homolytic dissociation of the NC bond (**$\mathrm{TS}_{\mathrm{DISS}}$**, 19 kcal mol^{-1}, $r_1 = 2.222$, see Scheme 4) to form a radical couple (**Cpl**, 20 kcal mol^{-1}). The diradicaloid character of this mechanism is testified by the $< S^2 >$ value (Table S6, Supporting Information) that grows from 0.50 for **$\mathrm{TS}_{\mathrm{DISS}}$** to 0.94 for **Cpl**. This step is followed by

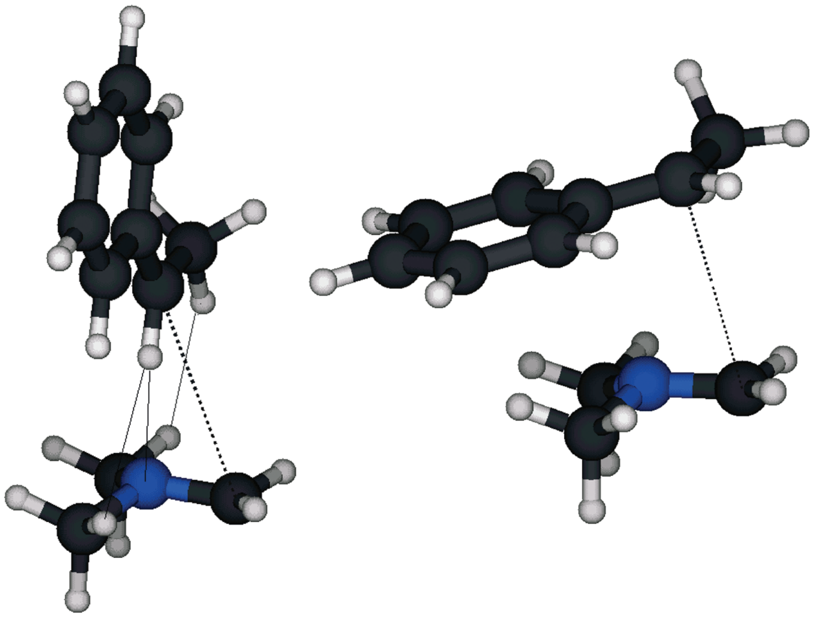
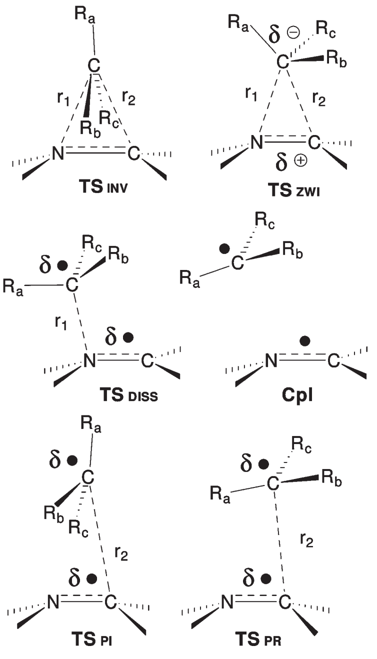


FIGURE 3. TS radical coupling with configuration inversion (left, $\mathrm{TS}_{\mathrm{PI}}$) and configuration retention (right, $\mathrm{TS}_{\mathrm{PR}}$) in the (1-phenylethyl)dimethylammonium ylide.

SCHEME 4. Relevant Structures in the Stevens Rearrangement



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, $<S^2>$ = 0.96); the other would lead to a product with retention of configuration (**TS$_{PR}$**, 23 kcal mol^{-1}, r_2 = 4.215, $<S^2>$ = 1.00). Both structures are very loose and show a strong diradical character as testified by the high $<S^2>$ values. It must be reported that in the case of **TS$_{DISS}$** the approximate spin projection scheme clearly overestimate the correction leading its energy below that one the complex. The error in the approximate spin projection for single point has already been underlined,[30h,i] suggesting caution in the comparison with values species with different, or any, spin contamination when energy differences are below 1−2 kcal mol^{-1}.

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}. This proces is favored in term of free energy by almost 20 kcal mol^{-1} due to the entropy gain (44 cal mol^{-1} K^{-1}).

TABLE 2. M05-2x Relative Energies (in kcal mol^{-1}) for the Stevens Rearrangement in the Tetramethylammonium Ylide in Solvents

	C_6H_{12}[a]	THF[b]	EtOH[c]	DMSO[d]	H_2O[e]
ylide	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] Dimethyl sulfoxide, ε = 46.7. [e] Water, ε = 78.4.

TABLE 3. M05-2x Relative Energies (in kcal mol^{-1}) for the Stevens Rearrangement in the Neopentyltrimethylammonium Ylide in the Gas Phase

	ΔE[a]	ΔE[b]	ΔG[c]
ylide	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.

With the introduction of solvent effects (Table 2), we observe that the free energies of the low-polarity radicals (dipole moment $\mu \approx 1$ D), **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 ylide (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 ylide. 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 ylide from neopentyltrimethylammonium (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

---

(34) Gaussian 03, Revision E.01: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian, Inc.: Wallingford, CT, 2004.

(35) Schaftenaar, G.; Noordik, J. H. Molden: a pre- and post-processing program for molecular and electronic structures. *J. Comput.-Aided Mol. Design* **2000**, *14*, 123–134.

(36) The BSSE error in the diradical complex for the single-point 6-311+G(3df,2p) is 0.27 kcal mol^{-1}.

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 ylide (**TS$_{DISS}$**, 13 kcal mol^{-1}, r_1 = 2.177, $<S^2>$ = 0.37) to form a radical couple (**Cpl**, 12 kcal mol^{-1}, $<S^2>$ = 0.96) followed by radical coupling through two alternative transition structures (**TS$_{PI}$**, 12 kcal mol^{-1}, r_2 = 3.254, $<S^2>$ = 0.95 and **TS$_{PR}$**, 17 kcal mol^{-1}, r_2 = 3.800, $<S^2>$ = 1.01) yielding the amine.

The neopentyltrimethylammonium ylide 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 neopentyl moiety (**TS$_H$**, 18 kcal mol^{-1}) yielding neopenthane and a new ylide ($CH_3N(CH_2)_2$). 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 ylide. Despite this result, we cannot exclude that **TS$_H$** could be reached from the ylide 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.

Several attempts to discover 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 ylide with **TS$_H$**. By contrast, the introduction of solvent effects (DMSO) already during the optimization[38] allowed us 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}, $<S^2>$ = 0.69). 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 ylide (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.

Therefore, the Stevens rearrangement in the ylide from neopentyltrimethylammonium 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.

TABLE 4. M05-2x Relative Free Energies (in kcal mol^{-1}) for the Stevens Rearrangement in the Neopentyltrimethylammonium Ylide in Solvents

	C_6H_{12}[a]	THF[b]	EtOH[c]	DMSO[d]	H_2O[e]
ylide	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] Dimethyl sulfoxide, ε = 46.7. [e] Water, ε = 78.4.

TABLE 5. M05-2x Relative Energies (in kcal mol^{-1}) for the Stevens Rearrangement in the Phenyltrimethylammonium Ylide in the Gas Phase

	ΔE[a]	ΔE[b]	ΔG[c]
ylide	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.

The Stevens rearrangement is the only reaction that can take place when the migrating group is aryl as in the ylide 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]

Differently from all other cases, a low-lying 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 ylide with the amine product without passing through any intermediate. This structure corresponds to a **TS$_{INV}$**, but at the variance of the other cases, it is stabilized by the delocalization of the negative charge (Figure S1, Supporting Information). The lack of hydrogen atoms bound to the migrating carbon and pointing toward the NC bond also combines to stabilize this structure. The low energy of **TS$_{MIG}$** compared to the free radicals (the phenyl cannot take advantage of any delocalization) led us to not fully explore the radical mechanism. Only the radical complex (**Cpl**, $<S^2>$ = 1.00) 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}.

Solvation effects (Table 6) are similar to previous cases, with radicals and **Cpl** (μ = 1.22 D) raised in free energy with respect to the ylide (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.

---

[37] Ess, D. H.; Wheeler, S. E.; Iafe, R. G.; Xu, L.; Celebi-Olcum, N.; Houk *Angew. Chem., Int. Ed.* **2008**, *47*, 7592–7601.

[38] Tests on the ylide from the neopentyltrimethylammmonium. 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.

	ΔE(a)	ΔE(b)	ΔG(c)
TS$_{DISS}$	24.4	19.5	15.2
TS$_{ZWI}$	38.7	37.8	31.4

TABLE 6. M05-2x Relative Free Energies (in kcal mol^{-1}) for the Stevens Rearrangement in the Phenyltrimethylammonium Ylide in Solvents

	C_6H_{12}[a]	THF[b]	EtOH[c]	DMSO[d]	H_2O[e]
ylide	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

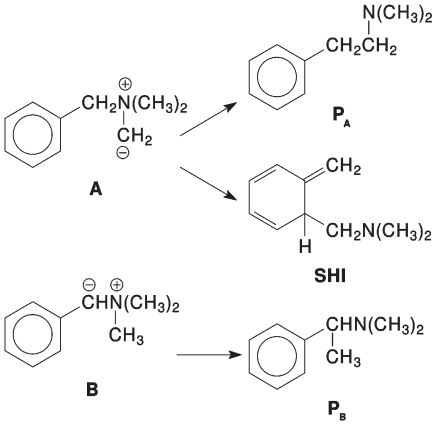
[a] Cyclohexane, ε = 2.0. [b] Tetrahydrofuran, ε = 7.6. [c] Ethanol, ε = 32.6. [d] Dimethyl sulfoxide, ε = 46.7. [e] Water, ε = 78.4.

TABLE 7. M05-2x Relative Energies (in kcal mol^{-1}) for the Stevens and Sommelet−Hauser Rearrangements in the Benzyltrimethylammonium Ylide in the Gas Phase

	ΔE[a]	ΔE[b]	ΔG[c]
ylide 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. intermediate	−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
elide 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.

SCHEME 5. Rearrangements in the Benzyltrimethylammonium Ylides



This is located 4 kcal mol^{-1} above $\mathbf{TS_{MIG}}$ both in term of electronic and free energies.[39] Because the formation of the ion couple would require overcoming 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 ylide from benzyltrimethylammonium (Schemes 1, 2: R = $C_6H_5-CH_2$, R_1 = R_2 = CH_3, Z = H; Scheme 5: **A**). This ylide can be obtained by abstraction of a proton from one of the methyl groups of the benzyltrimethylammonium. Another ylide, 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 ylides from the benzyltrimethylammonium only the Sommelet−Hauser rearrangement was observed,[10b,21,22] while in other studies both rearrangements were observed.[23a−c] Lepley reported on the role of the base and condition used to prepare the ylide from the ammonium salt[21b,23b] and put forward the hypothesis that the rearrangements are faster than ylide equilibration.[23c] It must be emphasized that in the experiments the Stevens product found is $\mathbf{P_B}$, which comes from the ylide **B** while the Sommelet−Hauser intermediate **SHI** comes from ylide **A**. Therefore, the latter only undergoes to Sommelet−Hauser rearrangement. The study of the ylide **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]

The study on the ylide **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; $\mathbf{TS_{INV}}$, μ = 3.97 D) was found at 21 kcal mol^{-1}. The delocalization of the charge in the benzyl moyety again stabilizes this structure (Figure S1, Supporting Information), however, as this time the effects is also present in the benzyl moyety the radical couple mechanism is the favored. This one passes again through the homolytic dissociation of the ylide ($\mathbf{TS_{DISS}}$, 8 kcal mol^{-1}, r_1 = 2.076, $<S^2>$ = 0.20) to a diradical complex (**Cpl**, 5 kcal mol^{-1}, $<S^2>$ = 0.98) followed by the two alternative pathways to recombination of the radicals($\mathbf{TS_{PI}}$, 8 kcal mol^{-1}, r_2 = 3.550, $<S^2>$ = 1.02 and $\mathbf{TS_{PR}}$, 8 kcal mol^{-1}, r_2 = 6.075, $<S^2>$ = 1.05). 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 ($\mathbf{TS_{IC}}$, 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 ($\mathbf{TS_{H}}$, 16 kcal mol^{-1}). As in the neopentyl case, this resulted from the IRC to connect the products (toluene and the ylide $CH_3N(CH_2)_2$) with the Stevens product and not with the initial ylide. However, also in this case we cannot exclude that this process could take place from the benzyl ylide as well. At variance

---

[39] Tests on the ylide 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.

	ΔE(a)	ΔE(b)	ΔG(b)
TS_{MIG}	19.0	18.6	16.8
Ion Couple	22.7	23.0	20.8

[40] Pine, S. H.; Cheney, J. *J. Org. Chem.* **1975**, *40*, 870–872.

TABLE 8. M05-2x Relative Free Energies (in kcal mol^{-1}) for the Stevens and Sommelet−Hauser Rearrangements in the Benzyltrimethylammonium Ylide at Different Temperatures (in °C) in the Gas Phase

	−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

TABLE 9. M05-2x Relative Free Energies (in kcal mol^{-1}) for the Stevens and Sommelet−Hauser Rearrangements in the Benzyltrimethylammonium Ylide in Solvents

	C_6H_{12}[a]	THF[b]	EtOH[c]	DMSO[d]	H_2O[e]
ylide 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. intermediate	−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
ylide 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] Dimethyl sulfoxide, ε = 46.7. [e] Water, ε = 78.4.

TABLE 10. M05-2x Relative Energies (in kcal mol^{-1}) for the Stevens and Sommelet−Hauser Rearrangements in the Phenacylbenzyldimethylammonium Ylide in the Gas Phase

	ΔE[a]	ΔE[b]	ΔG[c]
ylide	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. intermediate	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.

with the neopentyl 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.

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 ylide **A**/**B** interconversion.

In regard to the competition between the two rearrangements, we can observe that, in terms of free energy, the Sommelet−Hauser is hardly described as preferred over the Stevens by 0.2 kcal mol^{-1}. Clearly, this is not in full agreement with the experimental findings. However, the energy difference between the optimized relevant transition structures (TS_{DISS} and TS_{SH}) is not negligible (3.6 kcal mol^{-1}, Table 7, second column) but is reduced by 2 kcal mol^{-1} in the single-point calculations by the approximate spin projection which could overestimate the correction as observed in the tetramethylammmonium ylide.

Because the activation entropies (3.0 cal mol^{-1} K^{-1} for **TS_{DISS}** and 0.3 cal mol^{-1} K^{-1} for **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 five different temperatures. The effect is quite modest but shows a clear trend: a high temperature favors the Stevens rearrangement, as experimentally observed.[23d]

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 ylide (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.

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 = $C_6H_5CH_2$, 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.[40] Although this ylide gives both rearrangements, only the Stevens has been observed. The main effect of the phenacyl group is to stabilize the carbanion in the ylide, allowing less severe experimental conditions: sodium alkoxide in alcohols in lieu of sodium amide in liquid ammonia.

As a consequence of ylide 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 led us 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 charge" ions is even higher (167 kcal mol^{-1}).

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}** is 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}**.

TABLE 11. M05-2x Relative Free Energies (in kcal mol^{-1}) for the Stevens and Sommelet−Hauser Rearrangements in the Phenacylbenzyldimethylammonium Ylide in Solvents

	C_6H_{12}[a]	THF[b]	EtOH[c]	DMSO[d]	H_2O[e]
ylide	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. intermediate	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, $\varepsilon = 2.0$. [b] Tetrahydrofuran, $\varepsilon = 7.6$. [c] Ethanol, $\varepsilon = 32.6$. [d] Dimethyl sulfoxide, $\varepsilon = 46.7$. [e] Water, $\varepsilon = 78.4$.

TABLE 12. M05-2x Relative Energies (in kcal mol^{-1}) for the Stevens and Sommelet−Hauser Rearrangements in the (1-Phenylethyl)trimethylammonium Ylide in the Gas Phase

	ΔE[a]	ΔE[b]	ΔG[c]
ylide	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. intermediate	−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.

The solvent effects (Table 11) are consistent with the previous cases since we observe an increase of the relative free energies of radicals, $\mathbf{TS_{DISS}}$ ($\mu = 4.26$ D), **Cpl** ($\mu = 4.28$ D), $\mathbf{TS_{SH}}$ ($\mu = 3.49$ D), Stevens products ($\mu = 2.49$ D), and Sommelet−Hauser intermediate ($\mu = 2.84$ D) with respect to the more polar ylide ($\mu = 7.28$ 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.

The stereochemistry of the Stevens rearrangement has been frequently studied on 1-phenylethyl ylides.[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 ylide (Schemes 1 and 2: R = $C_6H_5CH(CH_3)$, $R_1 = R_2 = CH_3$, Z = H; Scheme 4: $R_a = C_6H_5$, R_b = H; $R_c = CH_3$; Table 12).

As in the previous cases, the homolytic dissociation of the CN bond ($\mathbf{TS_{DISS}}$, 6 kcal mol^{-1}, $r_1 = 2.013$, $\langle S^2 \rangle = 0.00$) to form the radical complex (**Cpl**, ~0 kcal mol^{-1}, $\langle S^2 \rangle = 0.96$) is the rate-determining step. Then, this step is followed by the two alternative pathways to recombination of the radicals ($\mathbf{TS_{PI}}$, 5 kcal mol^{-1}, $r_2 = 3.692$, $\langle S^2 \rangle = 1.03$ and $\mathbf{TS_{PR}}$, 2 kcal mol^{-1}, $r_2 = 3.558$, $\langle S^2 \rangle = 1.03$). The important difference with respect to the other cases is that the recombination path leading to retention of configuration ($\mathbf{TS_{PR}}$) is preferred by 2 kcal mol^{-1}. This result is qualitatively in accord with the experimental studies. The higher energy of $\mathbf{TS_{PI}}$ is probably due to the steric hindrance of the hydrogen atoms of the methyl group and the migrating carbon which are pointing toward the NC bond and the methyl hydrogen (2.6−2.7 Å: thin lines in Figure 3, left). This effect is not present (or sensibly reduced as distances are all above 3 Å) in $\mathbf{TS_{PR}}$ (Figure 3, right).

TABLE 13. M05-2x Relative Free Energies (in kcal mol^{-1}) for the Stevens and Sommelet−Hauser Rearrangements in the (1-Phenylethyl)trimethylammonium Ylide in Solvents

	C_6H_{12}[a]	THF[b]	EtOH[c]	DMSO[d]	H_2O[e]
ylide	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, $\varepsilon = 2.0$. [b] Tetrahydrofuran, $\varepsilon = 7.6$. [c] Ethanol, $\varepsilon = 32.6$. [d] Dimethyl sulfoxide, $\varepsilon = 46.7$. [e] Water, $\varepsilon = 78.4$.

The solvent effects (Table 13) do not change with respect to previous cases: we observe an increase of the relative free energies of radicals, $\mathbf{TS_{DISS}}$ ($p = 1.13$ D), **Cpl** ($p = 0.49$ D), $\mathbf{TS_{PI}}$ ($p = 1.57$ D), $\mathbf{TS_{PR}}$ ($p = 0.69$ D), and Stevens products ($p = 0.71$ D) with respect to the more polar ylide ($p = 5.37$ D). The free energy difference between $\mathbf{TS_{PI}}$ and $\mathbf{TS_{PR}}$ is always 2 kcal mol^{-1}. This substantial lack of dependence of this free energy difference on the solvent polarity is in agreement of the latest experimental evidence 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]

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 ylide ($\mathbf{TS_{DISS}}$) 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 ($\mathbf{TS_{PI}}$) and the other one to retention of configuration ($\mathbf{TS_{PR}}$). Steric considerations suggest that the latter can be slightly preferred in some 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 few radicals, often favored in term of free energy, cannot be excluded. Thus, 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 polar transition structure ($\mathbf{TS_{MIG}}$). 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. In all other cases (as in the benzyl system), the delocalization will stabilize both concerted and radical couple pathways with the latter favored.

The heterolytic pathway, when passing through a concerted zwitterionic transition structure ($\mathbf{TS_{ZWI}}$) 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 ylides (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.

Acknowledgment. Financial support by local funding by the University of Torino is gratefully acknowledged.

Supporting Information Available: Group charges for the concerted transition structures with retention; tabulated energies, entropies, dipole moments, and $<S^2>$ values (for diradicaloids only); Cartesian coordinates from DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.