J. Org. Chem. **1996,** *61,* 7276−7284

Competing Rearrangements of Ammonium Ylides: A Quantum Theoretical Study

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Received December 19, 1995 (Revised Manuscript Received July 30, 1996[⊗]*)*

The competition between the Stevens [1,2] and Sommelet−Hauser [2,3] rearrangements for a prototype ylide, *N*-methyl-3-propenylammonium methylide, has been investigated using *ab initio* and semiempirical molecular orbital methods. The activation energies for the two processes are remarkably close, separated by only 2 kJ mol^{-1} at ROMP/6-311+G(d,p). Increasing the size of the basis set leads to a relative stabilization of the Sommelet−Hauser transition geometry, while higher levels of electron correlation (such as CCSD(T)) favor the Stevens rearrangement. Incorporation of solvent effects via the SCRF polarizable continuum model leads to a lowering of the energy barrier of the concerted [2,3] rearrangement, but has little effect on the dissociative [1,2] pathway. The activation energies of both pathways have been calculated for ylides bearing substituents on the ammonium nitrogen and the double bond. Substituents at nitrogen lead to an ylide which is sterically unstable and hence a preference for the dissociative [1,2] rearrangement. Electron-withdrawing substituents on the double bond show a preference for the [2,3] rearrangement, while mildly electron-donating alkyl substituents have very little effect on activation energies.

Introduction

Ammonium ylides are important precursors in organic synthesis, due to their rearrangement under mild conditions to form highly substituted organic compounds and the ability to prepare stereospecific compounds from ammonium ylides. The major drawback in the use of ammonium ylides in synthesis is the competition between the two primary rearrangement pathways of these compounds, the Stevens [1,2] and the Sommelet−Hauser [2,3] rearrangements.

The Stevens rearrangement has been investigated as a synthetic route toward unnatural α-amino acid derivatives such as morpholin-2-ones[1] and in the synthesis of substituted piperidine rings.[2,3] Our theoretical studies on the Stevens rearrangement[4−7] have shown that the reaction proceeds via dissociation to a pair of radicals, followed by recombination to the product amine. There has been no indication of competition from a concerted pathway, nor the possibility of an ion pair being the dissociative intermediates.

The Sommelet−Hauser rearrangement is an attractive method for ring enlargement of cyclic amines[8,9] and in the formation of highly substituted benzylamines.[10] There has been little study of the transition geometry for the Sommelet−Hauser rearrangement, but since a concerted mechanism is permitted by symmetry, it is expected to be in effect.

Competition between the two rearrangements is the main drawback in the use of ammonium ylides in synthesis. In the case of ylides with a *β*-hydrogen, there is the added possibility of the Hofmann elimination to form an alkene and a less-substituted amine. There has been some experimental investigation into the effect of functional groups and stereochemistry on the ratio of rearrangement products;[9−12] however, there has been little theoretical study on the competing pathways.

In this study, we will use our previous *ab initio* and semiempirical calculations on ammonium ylides and the Stevens rearrangement as a basis for a study of the Sommelet−Hauser rearrangement. Comparison of the radical intermediates of the Stevens rearrangement with the concerted transition geometry of the Sommelet−Hauser rearrangement should give an indication as to which pathway is preferred and which orbital interactions are important in promoting each rearrangement pathway.

In this study, we have chosen to perform semiempirical and *ab initio* molecular orbital calculations on the competing rearrangement of a prototype ylide, *N*-methyl-3-propenylammonium methylide (**1**), shown in Figure 1. This ylide is particularly useful to our study since the Stevens and the Sommelet−Hauser rearrangement will give the same product amine, 4-(*N*-methylamino)-1-butene (**2**). This is particularly attractive for a theoretical study, in that any errors in calculation of the initial and final energies should fortuitously cancel out, and any activation energies calculated would be expected to be similarly affected by cancellation of errors. The Sommelet−Hauser rearrangement proceeds via transition geometry **3**, while the Stevens rearrangement involves two radical intermediates: the (*N*-methylamino)methyl radical **4** and the allyl radical **5**. Once the intermediates have been characterized, the important factors in each rearrangement will be taken into account by modifying

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[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1996.

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S0022-3263(95)02227-4 CCC: $12.00

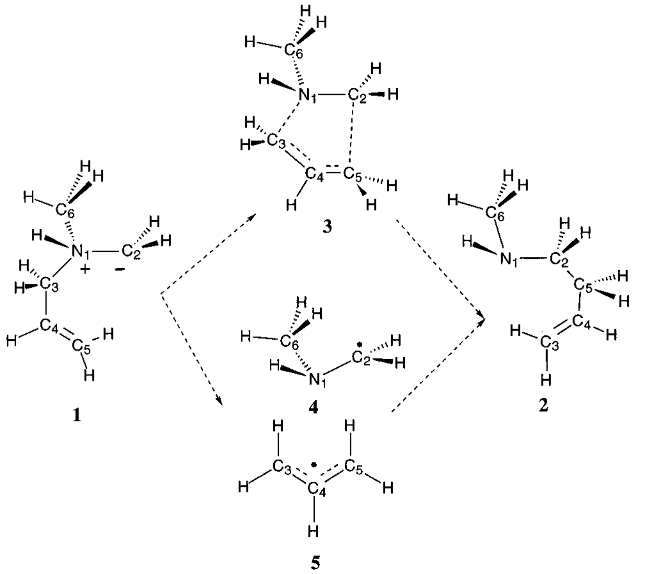

Figure 1. Competing rearrangements of *N*-methyl-3-propenylammonium methylide. Atom labels are used throughout the paper.

the skeleton so as to approach the ylides used in the experiment.

Methods

Standard *ab initio* and semiempirical calculations were carried out with the GAUSSIAN 92[13] and MOPAC 93[14] programs. The PM3[15] Hamiltonian has been used in semiempirical calculations, with the half-electron formalism for open-shell systems. Geometry minimizations at all levels have been performed using Baker's eigenvector following (EF) algorithm[16] where possible. *Ab initio* calculations use the following basis sets: 3-21G, 6-31G(d), 6-31+G(d), 6-311G(d), 6-311+G(d), 6-311+G(d,p).[17−20] .

Open-shell species have been treated at an *ab initio* level using both restricted Hartree−Fock (ROHF)[21] and unrestricted Hartree−Fock (UHF) formalisms. Electron correlation has been introduced through the Møller−Plesset theory,[22−25] with energy minimizations at second order (MP2) for both closed-shell and open-shell species. Due to the high degree of spin contamination in the radicals, energies have been calculated at the PUMP2[26] and ROMP2[27] levels on optimized UMP2 geometries. Core 1s electrons were frozen in all MP2 calculations. Higher levels of electron correlation have been taken into account with the coupled-cluster methods CCSD[28−31] and CCSD(T).[32]

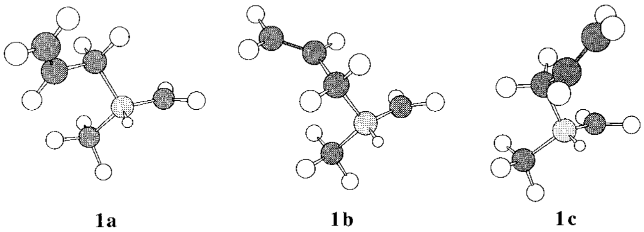

Figure 2. Structures of ylides **1a**−**c** optimized at PM3.

Table 1. Relative Energies (in kJ mol^{-1}) of Ylide Conformers

	ylide **1a**	ylide **1b**	ylide **1c**
PM3	0	5	6
RHF/3-21G	2	0	a
RHF/6-31G(d)	1	0	
MP2/6-31G(d)	2	0	

[a] No minimum corresponding to **1c** was located at the HF or MP2 level.

Electrostatic effects of solvation have been taken into account using the SCRF[33] formalism, a polarizable continuum method in which the molecule resides in a spherical cavity, the radius of which is determined from the molecular wave function.

Results

Geometries of Species. 1. *N*-methyl-3-propenylammonium Methylide. Determining the minimum-energy structure of organic molecules is often difficult, as there are several conformers possible, usually close in energy. It is also the case that low levels of theory sometimes predict the minimum energy conformation incorrectly, particularly in the case of substituted amines.[34] Since there is no spectroscopic or previous theoretical work on this particular ylide, a conformational analysis was carried out at the PM3 level of theory, and each local minimum found was optimized at the HF level with the 3-21G and 6-31G(d) basis set and at MP2/6-31G(d). Three local minima (**1a**−**c**, as shown in Figure 2) were located at PM3; however, at the HF level, no minimum corresponding to **1c** could be located. Relative energies at the four levels of theory are shown in Table 1. It can be seen that **1a** and **1b** are very close in energy, **1b** being slightly favored, and hence **1b** has been used as a starting point for all higher level calculations. Optimized bond distances, angles, and torsional angles for **1b** at the higher levels of theory are presented in Table 2.

Structures of ammonium ylides have attracted some attention in the literature.[35] This particular ylide has the characteristic long C−N bond distance. The double bond is aligned away from the lone pair on the carbanion, which puts it in an unfavorable position for the Sommelet−Hauser rearrangement.

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Table 2. Structural Parameters and Energies for Ylide 1b Optimized at MP2

	6-31G(d)	6-31+G(d)	6-311G(d)	6-311+G(d)	6-311+G(d,p)
N_1C_2	1.5259	1.5139	1.5212	1.5140	1.5145
N_1C_3	1.5168	1.5237	1.5157	1.5193	1.5175
C_3C_4	1.4973	1.4981	1.5000	1.5001	1.5007
C_4C_5	1.3410	1.3446	1.3421	1.3439	1.3438
N_1C_6	1.4832	1.4861	1.4817	1.4827	1.4828
$C_2N_1C_3$	117.8	117.8	117.4	117.6	117.5
$N_1C_3C_4$	113.8	113.4	113.7	113.3	113.4
$C_3C_4C_5$	122.5	122.4	122.5	122.4	122.2
$C_3N_1C_6$	111.2	110.6	110.9	110.4	110.7
$C_2N_1C_3C_4$	187.8	187.9	187.4	187.5	187.4
$N_1C_3C_4C_5$	99.14	95.84	97.82	95.16	96.57
$C_4C_3N_1C_6$	61.46	61.08	61.11	61.00	60.90
MP2/a.u.	−250.846518	−250.872795	−250.949152	−250.960833	−251.044600
CCSD	−250.913976				
CCSD(T)	−250.943282				
SCRF	−250.852432				−251.051184
a_0/Å	4.06				4.12

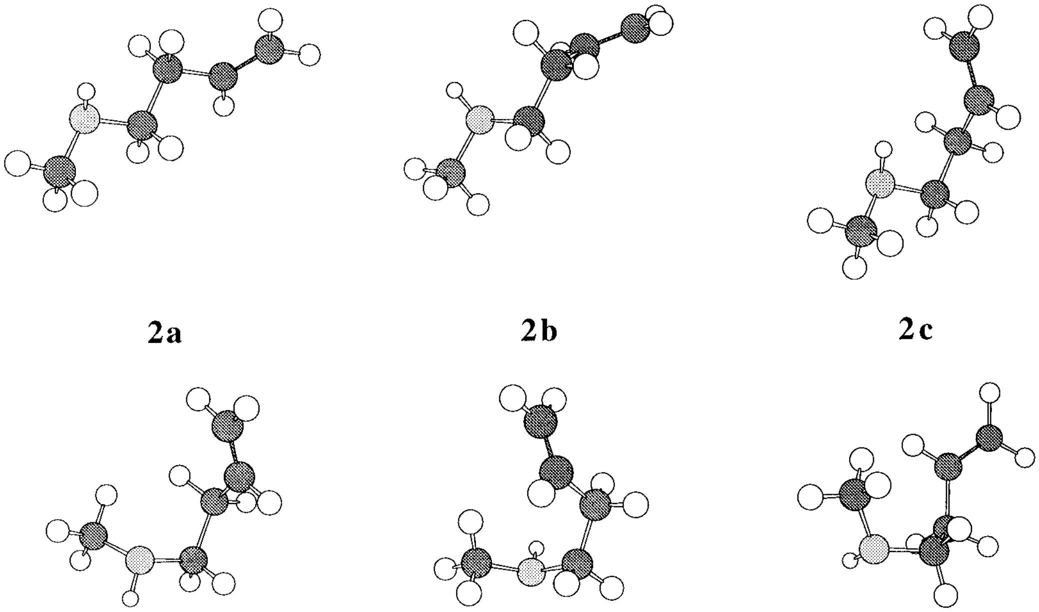
2a 2b 2c 2d 2e 2f

Figure 3. Structures of amines **2a**−**f** optimized at PM3.

Table 3. Relative Energies (in kJ mol^{-1}) of Amine Conformers 2a−f

	2a	2b	2c	2d	2e	2f
PM3	6	4	9	2	0	4
RHF/3-21G	0	1	9	13	14	4
RHF/6-31G(d)	2	0	10	15	18	2
MP2/6-31G(d)	4	0	8	15	18	5

2. 4-(*N*-methylamino)-1-butene. As with the ylide, a conformational search of the amine, using staggered conformations along the ($N_1C_2C_5C_4$) backbone as initial geometries, was carried out at the PM3 level, and six local minima were located, **2a**−**f** in Figure 3. Relative energies of all six conformations at PM3, RHF/3-21G, RHF/6-31G(d), and MP2/6-31G(d) are reported in Table 3. **2b** is predicted to be lowest in energy at MP2/6-31G(d), and all higher level calculations were carried out using this geometry as a starting point. Optimized MP2 geometries and energies for the amine are presented in Table 4. Although the amine is important for calculating reaction enthalpy, and in characterizing the correct transition geometry, there is no real insight into the competing rearrangements to be gained from calculations on the amine, as it is the reaction barriers that are more important. Since there is a large difference in energy between the ylide and the amine, the concerted transition geometry is expected to resemble the reactant more closely than the product.

3. Sommelet−Hauser Transition Geometry. The transition geometry for the Sommelet−Hauser rearrangement of **1b** to **2b** was located using the saddle-point algorithm of Dewar, Healy, and Stewart[36] and the PM3 Hamiltonian. Vibrational frequencies were calculated to verify the character of the saddle point, and the transition geometry was optimized to the ylide and amine by a slight increase and decrease in the $N_1C_3C_4$ bond angle. Optimized structural parameters and energies for the transition geometry **3** are presented in Table 5.

Just as there is a difference in the bond distances in ylide geometries depending on the method used to calculate them (PM3, HF, or MP2 wave functions), there is also a difference in the Sommelet−Hauser transition geometry, as seen in Figure 4. PM3 in particular predicts a much shorter bond distance in the ylide and hence allows for atoms C_2 and C_5 to become considerably closer

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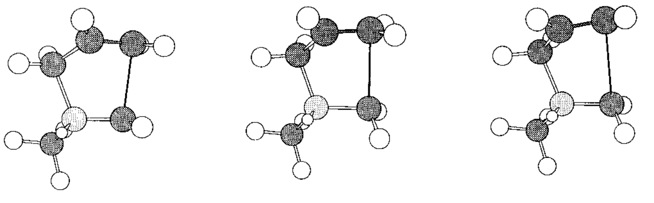
Table 4. Structural Parameters and Energies for Amine 2b Optimized at MP2

	6-31G(d)	6-31+G(d)	6-311G(d)	6-311+G(d)	6-311+G(d,p)
C_2N_1	1.4564	1.4577	1.4555	1.4556	1.4560
C_3C_2	1.5300	1.5302	1.5313	1.5312	1.5321
C_4C_3	1.5002	1.5004	1.5014	1.5014	1.5020
C_5C_4	1.3402	1.3436	1.3411	1.3429	1.3430
C_6N_1	1.4580	1.4603	1.4579	1.4581	1.4585
$C_3C_2N_1$	110.2	110.4	110.3	110.5	110.5
$C_4C_3C_2$	111.6	111.7	111.5	111.5	111.5
$C_5C_4C_3$	124.5	124.6	124.6	124.5	124.4
$C_6N_1C_2$	112.2	112.6	111.9	112.4	112.4
$C_4C_3C_2N_1$	65.92	65.14	65.69	64.94	65.44
$C_5C_4C_3C_2$	249.3	248.6	249.9	249.8	248.4
$C_6N_1C_2C_3$	185.0	183.1	183.1	182.7	184.8
MP2/a.u.	−250.962597	−250.979849	−251.056467	−251.065823	−251.149411
CCSD	−251.027493				
CCSD(T)	−251.055390				
SCRF	−250.960368				−251.149601
a_0/Å	4.06				4.10

Table 5. Structural Parameters and Energies for the Sommelet−Hauser Transition Geometry 3 Calculated at MP2

	6-31G(d)	6-31+G(d)	6-311G(d)	6-311+G(d)	6-311+G(d,p)
C_2C_5	2.7051	2.9586	2.7148	2.8727	2.8809
N_1C_2	1.4515	1.4315	1.4470	1.4369	1.4364
N_1C_3	1.6394	1.6759	1.6458	1.6681	1.6626
C_3C_4	1.4526	1.4563	1.4539	1.4559	1.4572
C_4C_5	1.3570	1.3550	1.3588	1.3560	1.3561
N_1C_6	1.4881	1.4888	1.4865	1.4838	1.4856
$C_2N_1C_3$	113.4	115.4	113.4	114.9	115.2
$N_1C_3C_4$	106.2	107.0	106.2	106.8	107.0
$C_3C_4C_5$	116.3	119.8	116.8	119.1	118.9
$C_3N_1C_6$	107.2	105.6	106.7	105.8	105.9
$C_2N_1C_3C_4$	302.8	303.9	304.2	307.9	306.2
$N_1C_3C_4C_5$	66.41	73.81	66.99	72.61	71.95
$C_4C_3N_1C_6$	171.4	174.9	173.6	180.2	177.3
MP2/a.u.	−250.833905	−250.858979	−250.935942	−250.947026	−251.031248
CCSD	−250.896258				
CCSD(T)	−250.928558				
SCRF	−250.836914				−251.034247
a_0/Å	4.04				4.10



PM3 RHF/3-21G MP2/6-31G(d)

Figure 4. Optimized Sommelet−Hauser transition geometries **3** at different levels of theory.

in the transition structure. At all levels, however, there are consistent differences between the ylide and the transition structure. The NC_3 bond, formally broken in the rearrangement, is lengthened in the transition geometry, and the NC_2 bond is shortened, consistent with the C−N charge-separated bond becoming a formal C−N single bond. The two angles NC_3C_4 and $C_3C_4C_5$ both tighten to allow C_5 and C_2 to come into position to form a bond, and there is a change in the dihedral angles which describe rotation about NC_3 and C_3C_4. There is little interaction between C_2 and C_5 in the transition geometry: the energy barrier seems to arise from rotating the molecule (in particular the double bond, which is in a sterically unfavorable environment) to a position where the bond formation occurs.

4. Stevens Rearrangement Intermediates. The structures and molecular energies of the Stevens rearrangement intermediates, the (*N*-methylamino)methyl radical, **4**, and the allyl radical, **5**, are presented in Tables 6 and 7, respectively. The structure of the amine radical is as expected from previous studies of amine radicals,[6] and the allyl radical has been well-characterized by experiment[37−39] and theory.[40,41] We have repeated the calculations in this study in order to make consistent comparisons with other species.

The allyl radical shows a high degree of spin contamination in the UHF and UMP2 wave function. In order to justify our single-point ROMP2 energy calculations on this structure, full geometry optimization has been carried out at ROMP2/6-31+G(d). The only geometry change was a slight lengthening of the C−C bond, and the difference in ROMP2 energy between the UMP2-optimized geometry and the ROMP2 geometry is only 0.3 kJ mol^{-1}. The geometries at all levels of theory are in good agreement with a recent experimental determination.[38]

Relative Energies. Relative energies for intermediates in each of the two rearrangements (in kJ mol^{-1} relative to amine **2**) are given in Table 8. At the PM3 level, the Stevens rearrangement is favored by 48 kJ mol^{-1}. This value is expected to be artificially large, since semiempirical methods overestimate the stability of open-

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Table 6. Structural Parameters and Energies of (*N*-Methylamino)methyl Radical 4 Calculated at MP2

	6-31G(d)	6-31+G(d)	6-311G(d)	6-311+G(d)	6-311+G(d,p)
C_2N_1	1.3940	1.3911	1.3908	1.3885	1.3886
C_6N_1	1.4553	1.4571	1.4546	1.4552	1.4553
$C_6N_1C_2$	117.1	117.7	117.2	117.7	117.6
$\langle s^2 \rangle$	0.7598	0.7618	0.7610	0.7622	0.7622
UMP2/a.u	−134.018928	−134.030886	−134.071384	−134.078633	−134.125687
PUMP2	−134.020633	−134.032736	−134.073193	−134.080520	−134.127582
ROMP2	−134.019204	−134.031216	−134.071695	−134.079001	−134.126150
CCSD	−134.055896				
CCSD(T)	−134.067274				
SCRF	−134.017707				−134.125697
a_0/Å	3.42				3.45

Table 7. Structural Parameters and Energies of the Allyl Radical 5 Calculated at MP2[a]

	6-31G(d)	6-31+G(d)	6-311G(d)	6-311+G(d)	6-311+G(d,p)	6-31+G(d)[b]
$H_{12}C_4$	1.0883	1.0890	1.0882	1.0884	1.0881	1.090
$H_{10}C_3$	1.0825	1.0830	1.0820	1.0822	1.0824	1.084
$H_{11}C_3$	1.0845	1.0852	1.0842	1.0844	1.0847	1.087
C_3C_4	1.3781	1.3806	1.3791	1.3803	1.3802	1.390
$C_3C_4H_{12}$	117.8	117.8	117.8	117.8	117.9	117.7
$H_{10}C_3C_4$	121.8	121.6	121.6	121.6	121.5	121.6
$H_{11}C_3C_4$	121.0	121.0	120.9	121.0	120.8	120.8
$\langle s^2 \rangle$	0.9606	0.9522	0.9554	0.9521	0.9509	
UMP2/a.u	−116.810216	−116.819168	−116.852147	−116.855480	−116.892630	
PUMP2	−116.824836	−116.833176	−116.866501	−116.869581	−116.906592	
ROMP2	−116.821064	−116.830281	−116.863695	−116.867176	−116.904958	−116.830385
CCSD	−116.856761					
CCSD(T)	−116.869524					
SCRF	−116.810217				−116.892631	
a_0/Å	3.38				3.42	

[a] Experimental values from ref 38 are $C_3C_4 = 1.3869$, $C_3C_4H_{12} = 118.02$. [b] Optimized ROMP2/6-31+G(d) parameters.

Table 8. Relative Energy of Rearrangements, in kJ mol^{-1} with respect to Amine 2b, at Various Levels of Theory.

	ylide **1**	Sommelet−Hauser **3**	Stevens (**4** + **5**)
PM3	224	275	227
UHF/3-21G	292	360	182
ROHF/3-21G			257
UHF/6-31G(d)	315	399	187
ROHF/6-31G(d)			263
UMP2/6-31G(d)	306	338	350
PUMP2[a]			308
ROMP2			325
UMP2/6-31+G(d)	281	317	341
PUMP2			299
ROMP2			311
UMP2/6-311G(d)	281	316	349
PUMP2			307
ROMP2			318
UMP2/6-311+G(d)	276	312	346
PUMP2			304
ROMP2			314
UMP2/6-311+G(d,p)	275	310	344
PUMP2			303
ROMP2			312
CCSD/6-31G(d)[b]	298	345	301[c]
CCSD(T)/6-31G(d)[b]	294	333	311[c]

[a] PUMP2 and ROMP2 energies calculated at the appropriate optimized MP2 geometry. [b] Calculated at optimized MP2/6-31G(d) geometry. [c] Calculated at optimized UMP2/6-31G(d) geometry.

shell species. The HF methods predict the Stevens rearrangement to be favored by over 100 kJ mol^{-1}; again, HF is an inappropriate method for comparison of a pair of radicals with a closed-shell concerted rearrangement, and there is expected to be considerable correlation energy in all species. At MP2/6-31G(d), the Stevens rearrangement is favored by 30 kJ mol^{-1} at PUMP2 and 13 kJ mol^{-1} at ROMP2. As this energy separation is quite small, the effects of further correlation and larger basis sets have been investigated.

Increasing the flexibility of the basis set (by adding further primitives, polarization, and diffuse functions) has the effect of lowering the relative energy of the Sommelet−Hauser rearrangement at MP2, as seen in Table 8. The effect on the radicals is a slight lowering in relative energy, not as pronounced as in the concerted process. The activation energy of the Stevens rearrangement is raised as the basis set increases, while the activation energy of the Sommelet−Hauser process remains much the same. MP2 optimizations at the largest basis set, 6-311+G(d,p), involving polarization on all of the hydrogen atoms, predict the Stevens rearrangement to be favored by 7 kJ mol^{-1} at PUMP2, but the Sommelet−Hauser rearrangement to be favored by 2 kJ mol^{-1} at the ROMP2 level. In general, larger basis sets tend to favor the Sommelet−Hauser rearrangement over the Stevens rearrangement.

Further electron correlation effects were taken into account by calculations at the CCSD(T)/6-31G(d) level using the optimized MP2/6-31G(d) geometries. The activation energy of the Stevens pathway is lowered considerably; there is little change in the Sommelet−Hauser activation energy. Thus higher levels of electron correlation seem to favor the Stevens rearrangement over the Sommelet−Hauser rearrangement.

Solvation effects have been shown to have a minor effect on the activation energy of the Stevens rearrangement;[7] however, the effect on the [2,3] transition geometry is unknown. To investigate the electrostatic effects of solvation, SCRF energies have been calculated at the MP2/6-31G(d) level, with dielectric constant values of $\epsilon = 2.95$ (corresponding to THF), $\epsilon = 30.0$ (corresponding to HMPA), $\epsilon = 35.9$ (acetonitrile), $\epsilon = 36.7$ (DMF), and $\epsilon = 78.5$ (water—although not a common solvent in this type of rearrangement, it is worth including to see an extreme case of solvent polarizablility). The relative energies are shown in Table 9. Although there are some

Table 9. Relative SCRF Energies (in kJ mol^{-1} from Amine 2) for Rearrangement of 1 at MP2/6-31G(d)

solvent	ϵ	ylide (**1**)	Sommelet−Hauser (**3**)	Stevens (**4** + **5**)
none	1.0	306	338	350
THF	2.95	290	327	348
HMPA	30.0	284	324	348
CH_3CN	35.9	283	324	348
DMF	36.7	283	324	348
H_2O	78.5	283	324	348
CH_3CN^a	35.9	258	303	345

[a] MP2/6-311+G(d,p) SCRF energy calculated at optimized UMP2/6-311+G(d,p) geometry.

small changes in going from the gas phase to a low polarity solvent and then to one of higher polarity (such as HMPA), there is little additional electrostatic effect from solvents with a large dielectric constant. As a final test of solvation, the SCRF energies were calculated at MP2/6-311+G(d,p) (the basis set recommended by Wong[33] for SCRF calculations), and essentially the same difference in relative energies was found. There is little effect on the relative energies of the radical species at either level of theory; however, the relative energy of the Sommelet−Hauser rearrangement intermediate is lowered slightly. Since there is a large change in the molecular energy of the ylide, there is an overall increase in activation energy for both pathways; however, the Sommelet−Hauser rearrangement appears to be favored by the inclusion of the electrostatic effects of solvation.

One other effect which may be important in determining the relative energy of these two processes is the difference in entropy, due to the formation of two intermediate species in the Stevens rearrangement and only one intermediate species in the Sommelet−Hauser. However these entropy effects in the intrinsic reaction are likely to be less important than the entropy effects arising from solvation of these ionic species, and both effects should be treated together in a more complete model.

It is of interest to try to compare the relative energies calculated here with any available experimental information. The experimental heat of formation of **5** has been determined very recently as $\Delta H_{f,298} = 41.5 \pm 0.4$ kcal mol^{-1},[39] while $\Delta H_f(\mathbf{4}) = 30 \pm 2$ kcal mol^{-1}.[42] As the experimental value for **2** is unknown, we have estimated $\Delta H_{f,298}(\mathbf{2}) = 8.1$ kcal mol^{-1} from an MM3[43,44] calculation which should be accurate to ±5 kcal mol^{-1}. Thus $\Delta E(\text{Stevens}-\text{amine}) = (\Delta H_f(\mathbf{4}) + \Delta H_f(\mathbf{5}) - \Delta H_f(\mathbf{2})) \approx 63.4 \pm 7.4$ kcal mol^{-1} $= 265 \pm 31$ kJ mol^{-1}. On comparing this result with the values in the final column of Table 8, it appears that the *ab initio* values are too high but that they are converging toward the upper bound of the experimental number. Clearly a more accurate determination of the experimental heats of formation of **4** and **2** is desirable before drawing firm conclusions.

Substituent Effects. Now that the two sets of intermediates have been characterized, it is clear that they are very close in energy, with larger basis sets and more electron correlation tending to act in opposite ways. In order to investigate what causes the experimental preference for one rearrangement over the other, this prototype rearrangement has been modified by substituting selected hydrogens with other functional groups.

Since the Stevens rearrangement is radical in nature, ylides which dissociate to form stable radicals would be expected to prefer the Stevens rearrangement. Ylides which are very unstable would also tend to favor breaking of the NC_3 bond to form the required radical fragments. However, since this bond is also broken in the Sommelet−Hauser rearrangement, choosing an ylide which will dissociate easily may not cause the Stevens pathway to become any more preferred than the Sommelet−Hauser pathway.

In the transition geometry of the Sommelet−Hauser rearrangement, the lone pair on the carbanion C_2 must be able to orient itself with the empty π^* antibonding orbital corresponding to the C_4C_5 double bond. It is possible that this could be done sterically, using rigid cyclic systems, electronically, by delocalizing the C_4C_5 double bond and promoting its rotation, or by raising the energy of the lone pair on C_2 and thus encouraging bond formation of some description. Using electron-withdrawing groups to stabilize the lone pair could have the effect of raising the activation energy of the Sommelet−Hauser rearrangement and thus causing a preference for the Stevens rearrangement. Heavily localizing the double bond and making its rotation unfavorable could have the same effect.

In order to investigate these possibilities, a study of substituent effects, involving a variety of electron-withdrawing and electron-donating groups replacing the hydrogen atom attached to N_1 (being β to the lone pair on C_2) and the hydrogen atom attached to C_4 (being β to C_5), has been undertaken at the PM3 level of theory. The absolute energies are not expected to be reliable, for the reasons seen in the study of the prototype rearrangement system; however, our previous studies on ammonium ylides[7] show that the trends in energies across a range of substituents should be similar to those predicted by *ab initio* calculations. Calling our original rearrangement of **1** → **2** rearrangement **A**, the substituted rearrangements are **B**−**O**. The Sommelet−Hauser transition geometries are presented in Figure 5, and the relative energies for each rearrangement calculated at PM3 are presented in Table 10.

1. Substitution at N. Experimentally, direct substitution at N would be a difficult process. In most syntheses, groups directly substituted at N are alkyl or aryl in nature. The effect of all substituents at N (with the exception of NH_2) is a considerable lowering of the activation energy of the Stevens rearrangement. This is most likely due to highly substituted ylides being sterically, as well as electronically, unstable: dissociation to radicals would most likely occur with no energy barrier. Electron-withdrawing groups on N show no clear trend with regard to the relative energy of the Sommelet−Hauser rearrangement; CN, NH_2, and CHO each stabilize the ylide relative to the Sommelet−Hauser transition geometry; however, all substitutions at N indicate an increased preference for the Stevens rearrangement over the Sommelet−Hauser rearrangement.

Looking at this from the point of view of molecular geometries, most substituents on N give rise to geometry changes in the Sommelet−Hauser transition state. The NC_3 bond is slightly longer in all cases, accompanied by a smaller C_2NC_3 angle, indicating that the transition state occurs further along the reaction pathway than in the unsubstituted case. Again, these changes are con-

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(42) Griller, D.; Lossing, F. P. *J. Am. Chem. Soc.* **1981**, *103*, 1586.

(43) Schmitz, L. R.; Allinger, N. L. *J. Am. Chem. Soc.* **1990**, *112*, 8307.

(44) This calculation is for the global minimum, and no attempt has been made to take into account a true Boltzmann average. Equivalent calculations of the global minima at the AM1 and PM3 levels of theory give estimates for the heat of formation of **2** of 5.3 and 5.0 kcal mol^{-1}, respectively.

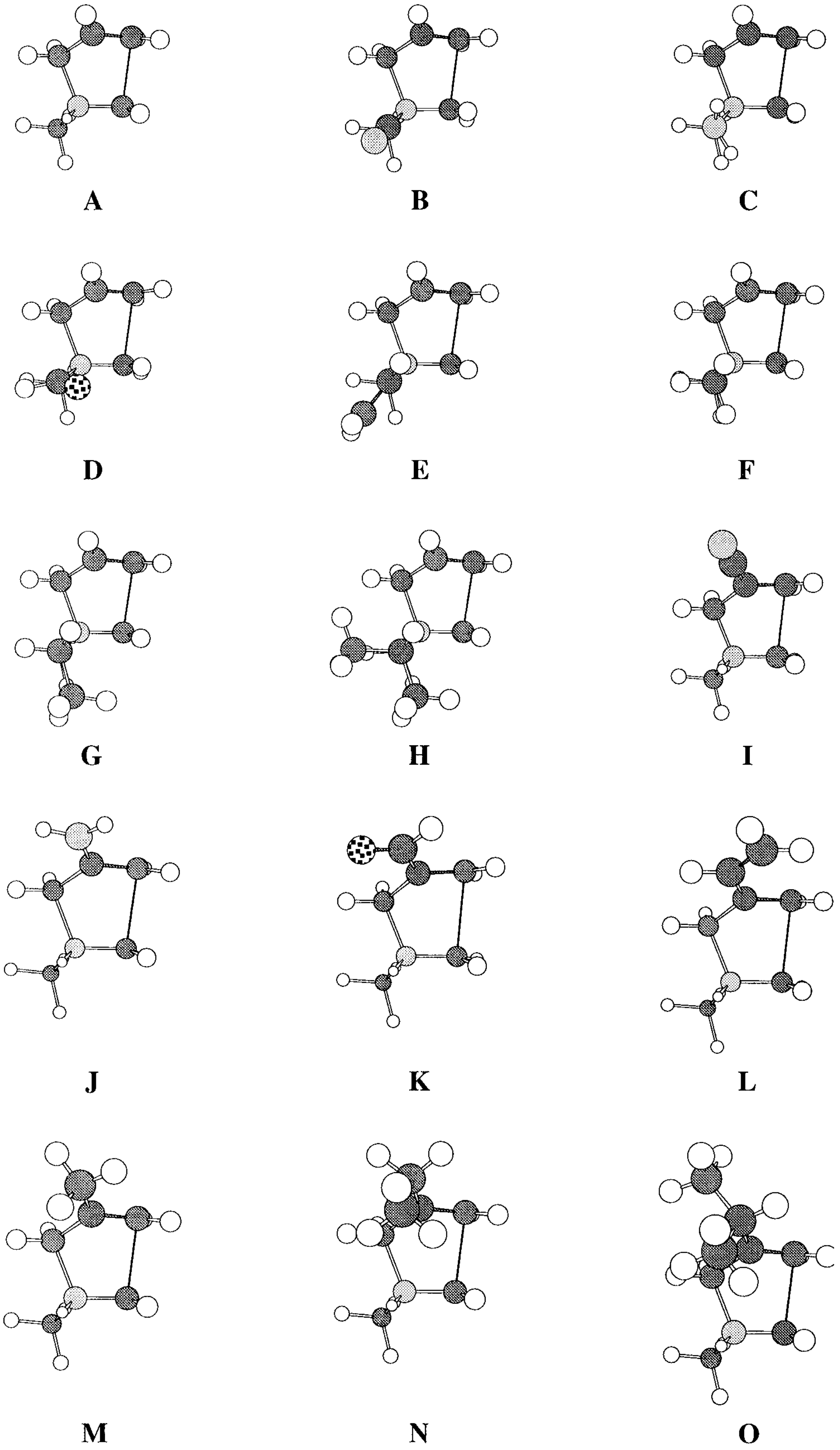

Figure 5. PM3 optimized geometries of substituted Sommelet−Hauser transition geometries for rearrangements **A**−**O**.

sistent with a higher degree of steric instability of the ylide and are reflected in the facility of dissociation to the Stevens radical.

2. Substitution at C_4. Inspection of the relative energies of pathways involving substitution at C_4 shows a number of interesting results. The substituents have very little effect on the activation energy of the Stevens rearrangement. This is to be expected, since the substituents are far enough removed from the NC_3 bond as to have little effect on the strength of that bond. Electron-withdrawing groups (with the exception of NH_2) lower the activation energy of the Sommelet−Hauser rear-

Table 10. Relative Energies of Competing Pathways (in kJ mol^{-1} with Respect to Ylide) for Rearrangements A–O at PM3

ylide	N-sub	C_4-sub	ΔE-(Stevens)	ΔE-(S-H)	ΔE-(S-H−Stevens)
A	H	H	4	51	47
B	CN	H	−19	60	79
C	NH_2	H	1	60	59
D	CHO	H	−48	51	99
E	$CH{=}CH_2$	H	−36	33	69
F	CH_3	H	−26	37	63
G	CH_2CH_3	H	−30	37	67
H	$CH(CH_3)_2$	H	−31	37	68
I	H	CN	1	25	24
J	H	NH_2	9	54	45
K	H	CHO	4	22	18
L	H	$CH{=}CH_2$	2	36	34
M	H	CH_3	7	52	45
N	H	CH_2CH_3	4	44	40
O	H	$CH(CH_3)_2$	4	46	42

Table 11. Relative Energy of the Sommelet–Hauser Transition Geometry (in kJ mol^{-1} with Respect to the Stevens Transition Intermediates) at Various Levels of Theory

	PM3	UHF/ 6-31G(d)	ROHF/ 6-31G(d)	UMP2/ 6-31G(d)	ROMP2/ 6-31G(d)[a]
A	47	212	136	−12	13
B	79	290	213	32	63
F	63	233	156		
I	24	166	79	−70	−24
M	45	229	151		

[a] Calculated at the UMP2/6-31G(d) geometry.

rangement considerably; however, electron-donating groups have little effect on the Sommelet–Hauser rearrangement barrier. This can be rationalized in terms of the double bond between C_4 and C_5. The presence of electron-withdrawing groups on C_4 would reduce the double-bond character and allow more freedom of rotation, which is required for C_2 and C_5 to come into alignment for the Sommelet–Hauser rearrangement. Electron-donating groups may be expected to localize the double bond and hinder rotation; however, that effect is not seen with the mildly electron-donating groups studied here.

Inspection of the geometries of these species supports this hypothesis. The C_4C_5 bond is slightly longer in the substituted ylides, an indication of increased delocalization. The C_3C_4 bond is also longer. The Sommelet–Hauser transition is an earlier transition structure, with a more open C_2NC_3 and NC_3C_4 angle.

3. Ab Initio Studies of Substitution. The *ab initio* optimization of rearrangements **B**–**O** is, in general, beyond the computational power available. Single-point MP2/6-31G(d) calculations on the optimized PM3 geometries, which have been shown to be useful in comparing energies of the Stevens rearrangement,[7] would be possible, yet impractical as there are great differences between the PM3 and MP2/6-31G(d) optimized geometries involved in the [2,3] rearrangement of **A**, and hence the single-point energies would be unreliable.

In an attempt to have some *ab initio* results to back up the PM3 findings, transition geometries for **B** and **I** (involving a nitrile group) and **F** and **M** (involving a methyl group) have been optimized at RHF/6-31G(d). Rearrangements **B** and **I** were also optimized at MP2/6-31G(d). Relative energies for the transition structures are given in Table 11.

At MP2/6-31G(d), rearrangements **B** and **I** show the same behavior as they did at PM3. The difference in energy between the two pathways is increased in the case of electron-withdrawing functionality at N and decreased when the nitrile group is coordinated to the double bond. The NC_3 bond is longer in **B**; however, it is the NC_3C_4 angle which is tighter. In **I**, the Sommelet–Hauser transition structure resembles **A**, and at MP2/6-31G(d) it is predicted to be considerably favored over the Stevens (recall that in **A** the Sommelet–Hauser was favored at UMP2, and the Stevens at ROMP2).

For methyl substitution (**F** and **M**), there is little real change to the energy differences, consistent with the trend seen at PM3. In each case the Stevens rearrangement is slightly favored compared to **A**. The concerted transition geometries of **F** and **M** are very similar along the skeleton, both resembling more the substituted N geometries than the substituted double-bond geometries.

In summary, at the *ab initio* level of theory, a nitrile substituent at N favors the Stevens rearrangement, a nitrile substituent at C_4 favors the Sommelet–Hauser, and a methyl substituent at either of these positions has little effect.

Although there have been a number of complementary experimental studies on the competition between the Sommelet–Hauser and Stevens mechanisms,[9–12] these studies employed aromatic rings to provide the participating C=C double bond (with a consequent modification in the reaction mechanism), and substituent effects were only investigated as far as substitution on the aromatic ring was concerned.[11] Direct comparisons with our work are difficult; however, it was found in these experiments that electron-deficient aromatic systems favored the Sommelet–Hauser rearrangement,[12] which is consistent with our conclusions about the effect of electron-withdrawing groups. Further theoretical work is required on our part to model these more complex experimental systems.

Conclusions

The competing transition geometries for both the [1,2] (Stevens) and [2,3] (Sommelet–Hauser) rearrangements of *N*-methyl-3-propenylammonium methylide have been characterized at semiempirical and *ab initio* levels of theory. The Stevens rearrangement intermediates are the two radical species (as predicted in previous work). The Sommelet–Hauser intermediate involves orienting the lone pair of the carbanion with the double bond in preparation for the formation of a carbon–carbon bond, and hence the barrier to the Sommelet–Hauser rearrangement is primarily controlled by steric factors. Electronic effects are important in determining geometries and hence can influence the steric effects.

The two rearrangements are predicted to be very close in energy. Too close, indeed, to assign a preferred mechanism for this particular ylide. Increasing the size of the basis set shows a preference for the concerted [2,3] rearrangement, while increased levels of electron correlation show a stabilization of the radical rearrangement. Calculations including the electrostatic effects of solvation using the SCRF formalism show a stabilization of the concerted transition structure.

Investigation of the effects of substitution on this prototype rearrangement show that the degree of preference can be influenced by the functional groups present. The preference for the Stevens rearrangement occurs when there is an unstable onium part of the ylide assisting the breaking of the N−C bond before rotation. This is achieved with substitution of the amine causing a sterically favored dissociation. The Sommelet−Hauser rearrangement can be promoted by delocalization of the double bond involved in the rearrangement, since this bond has to rotate somewhat (and effectively lose its double-bond character). This seems to be favored by electron-withdrawing substituents on the double bond. This would concur with the experimental evidence where there are typically several electron-donating and electron-withdrawing substituents around the aromatic ring. The effects of electron-donating groups are difficult to consider theoretically; however it is probable that electron-donating groups could localize the double bond and hinder the formation of the concerted transition structure.

In summary, although we have been unable to identify clear factors which favor one rearrangement over another, we have shown that at various levels of theory for a variety of ylides these two rearrangements are evenly poised. This in itself is a significant finding, and the computational study of such competing rearrangements is worthy of future investigation.

Acknowledgment. The authors thank the Australian National University Supercomputing Facility (ANUSF), the Australian Institute of Nuclear Science and Engineering (AINSE) and the University of Tasmania for generous allocations of computer time, and the Australian Research Council for funding this project.

Supporting Information Available: Tables of bond lengths optimized at PM3 and HF/6-31G(d) for the ylides and Sommelet−Hauser transition geometries involved in rearrangements **A**−**O**, together with a complete *Z*-matrix at PM3 (and MP2/6-31G(d) where available) for every significant species studied in this investigation (99 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO952227W