

Ab Initio Calculations of [1,2]-Shifts in Carbanions. Theoretical Predictions of Certain Facile Rearrangements

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Received December 2, 1997

The activation barriers for the [1,2]-migration of several groups in acetylide anions, i.e., $\text{RC}_\alpha\equiv\text{C}_\beta^- \rightarrow ^-\text{C}_\alpha\equiv\text{C}_\beta\text{R}$, were calculated with ab initio methods. The barrier for the rearrangement depends on the capability of R to form a hypervalent-type bonding, for which its ability to accomplish negative hyperconjugation as well as its polarizability are important. For these reasons, substituents derived from second-row elements are significantly better migrating groups than their first-row counterparts. The gas-phase acidity of the acetylenes $\text{RC}\equiv\text{CH}$ was found to be dependent mainly on the inductive and resonance effects of R; influence of negative hyperconjugation and polarizability were also observed. Some migrations in the ethenyl ($\text{RCH}=\text{CH}^-$) and ethyl ($\text{RCH}_2\text{CH}_2^-$) anions were also calculated. The major finding was that the barriers for the migration of SiH_3 , GeH_3 and AlH_2 in $\text{RC}\equiv\text{C}^-$ are relatively low and these hitherto unknown rearrangements should presumably be observed experimentally. Moreover, silicon, which has only been found to migrate in saturated carbanions, could do so also in vinylic anions.

Introduction

Anionic rearrangements involving migration of groups are known to occur in species containing heteroatoms.^{1a,2} Examples of this type of reactions are the Wittig,³ Wright–West,⁴ and Brook⁵ rearrangements, as well as ylide rearrangements (Stevens, Meisenheimer, etc.),^{1a} where the migration of a group involves its bonding to the heteroatom. However, very rare cases of anionic shifts between carbon atoms have been reported in the literature.^{6,7} There are no definite examples of concerted carbanionic [1,2]-alkyl shifts, as well as no proved examples of intramolecular [1,*n*]-alkyl shifts or of the corresponding intermolecular processes. Similarly, no cases involving [1,2]-hydrogen migration along a carbanionic carbon chain are known, the [1,3] and more remote migrations being equally unusual.

This intriguing feature regarding the chemical behavior of carbanions containing only carbon and hydrogen is in sharp contrast with the commonly observed rearrangements of carbenium ions.^{1b} This interesting dif-

ference between carbanions and carbenium ions has been explained by the Woodward and Hoffmann orbital symmetry rules.⁸ Thus, concerted carbanionic [1,2]-migration of saturated alkyl groups or hydrogen are forbidden as suprafacial–suprafacial processes but are allowed as suprafacial–antarafacial processes (Scheme 1);^{6b} nevertheless, such antarafacial transition states appear unlikely because of steric difficulties. Similarly, Zimmerman and Zweig had concluded that alkyl migrations in carbanions could only be observed under extreme conditions.^{9a} On the other hand, in carbenium ions, [1,2]-shifts are allowed when both components occur suprafacially and these reactions are hence facile.

The few examples of systems that undergo [1,2]-anionic shifts between carbon atoms include mostly migration of aryl and vinyl groups across a single C–C bond. Among them there is the so-called Grovenstein–Zimmerman rearrangement, in which $\text{Ph}_3\text{CCH}_2\text{Cl}$ treated with sodium gives $\text{Ph}_2\text{CHCH}_2\text{Ph}$ along with unrearranged products. The intermediate is $\text{Ph}_3\text{CCH}_2^-$, and the phenyl group moves without its electron pair. Only aryl, vinylic,^{10a} and acetylenic^{10b} groups migrate by this mechanism, while migration of alkyl groups has not been observed.

There is also limited experimental evidence concerning [1,2]-migrations of acetylenic, carbonyl, and alkoxy-carbonyl groups.^{6,7} Nevertheless, those processes involving unsaturated groups were claimed to be favored by molecular orbital considerations.⁹ In these cases the negative charge in the transition state delocalizes through the

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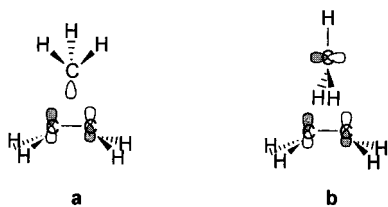
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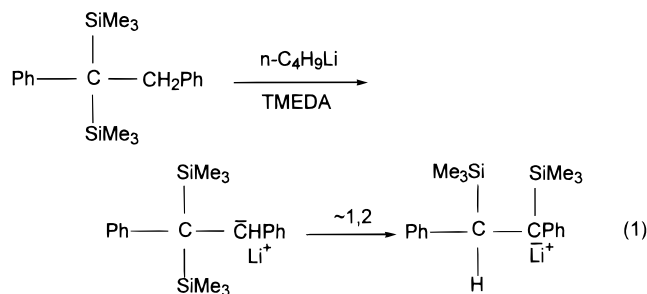
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Scheme 1 [1,2]-Methyl Migration^a

^a (a) Suprafacial-suprafacial process. (b) Suprafacial-antarafacial process.

π -system of the migrating group and, consequently, the energy barrier for such rearrangements is lower.

All first-row substituents ($R = \text{BH}_2, \text{CH}_3, \text{NH}_2, \text{OH}, \text{F}$) suffer the same orbital symmetry constraints for migration. Although migration with inversion of configuration at R is an allowed process, experimental examples of its occurrence appear to be unknown.⁷ Anyway, a BH_2 group would provide a lower energy pathway for [1,2]-shift via a four-coordinate boron intermediate; in this case orbital symmetry restrictions are avoided, but examples of such process are not known. Formation of the cyclic species required for [1,2]-migration should also be energetically favored for other elements having vacant orbitals in the valence shell, i.e., elements other than those in the first row of the periodic table, as vacant orbitals would confer "unsaturated" character. However, silicon provides the only example to date of such a rearrangement. A trimethylsilyl (TMS) group was found to migrate between carbanionic sites under mild conditions (25 °C) in preference to a phenyl ring (reaction 1):^{11a}



Other [1, n]-TMS migrations were subsequently observed in similar systems.^{11b-d} [1,4]-TMS shifts have also been observed in 9,10-dihydroanthracene anions.¹² The driving force of these rearrangements was attributed to the ability of silicon atoms to pentacoordinate by using empty d-orbitals to bear the negative charge.^{12e,13}

Theoretical calculations concerning anionic species have increased in number especially after it was realized by Schleyer et al. that the use of diffuse-function augmented basis sets provided more reasonable results.¹⁴

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Diffuse functions are required to adequately describe structural and energetic properties of anions, due to the weakly bound nature of the extra electron. The above observations about the difficult attainment of [1,2]-shifts in carbanions have been supported by ab initio molecular orbital calculations for the [1,2]-hydrogen shift on the ethyl ($\text{CH}_3\text{-CH}_2^-$), ethenyl ($\text{CH}_2=\text{CH}^-$) and ethynyl ($\text{HC}\equiv\text{C}^-$) anions.¹⁵ At the MP3/6-31++G**//6-31+G* level of theory the barriers for the rearrangement were high for the ethyl (51.6 kcal/mol) and ethenyl (63.8 and 59.5 kcal/mol) systems. Interestingly, the barrier for the ethynyl anion was only 21.3 kcal/mol.

The purpose of this study was to computationally find carbanions that can undergo [1,2]-shifts under mild conditions and to point them out to experimentalists. As the lowest barrier had been calculated for $\text{HC}\equiv\text{C}^-$, acetylide anions were focused on. The second goal was to rank the migratory ability in anionic rearrangements of the standard first- and second-row substituents.

Computational Methods

Standard ab initio calculations were performed employing the Gaussian 94 series of programs.¹⁶ Geometry optimizations were carried out at the Hartree-Fock (HF) level by applying gradient-optimization procedures¹⁷ using the diffuse and polarization-function augmented 6-31+G* split-valence shell basis set.^{14b,18} The 6-31+G* optimized geometries were used for single-point calculations at the third-order Møller-Plesset perturbation correction (MP3)¹⁹ for treatment of electron correlation effects. Further discussion will consider those values obtained at the highest level of theory. Transition states were located with the eigenvector-following (EF) optimization routine.²⁰

To characterize stationary points as minima (equilibrium structures, no imaginary frequencies) or first-order saddle points (transition structures, one imaginary frequency) and to include the effects of zero-point vibrational energies in estimating the relative energies of the structures, harmonic vibrational frequencies were calculated at the HF level with the 6-31+G* basis by using geometries optimized with that basis set. In the case of geometries optimized at the MP2 level or with basis sets other than 6-31+G*, harmonic vibrational frequencies were calculated at the same level and with the same basis set used for the optimization procedure.

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For calculations involving Ge, standard Huzinaga–Dunning²¹ double- ζ basis sets on hydrogen and carbon atoms and the Olbrich contraction²² of Dunning's 13s9p5d set²³ of primitive Gaussian orbitals on the germanium atom were used. These were augmented by single polarization functions for every atom with exponents $d_{\text{Ge}} = 0.50$; $p_{\text{H}} = 0.75$; $d_{\text{C}} = 0.75$. The contraction schemes were Ge (13s9p6d/7s5p4d), H (4s1p/2s1p), C (9s5p1d/4s2p1d). For comparison, calculations on the anionic systems substituted by SiH₃ and AlH₂ were performed employing also the standard Huzinaga–Dunning double- ζ basis sets. The contraction schemes were Si (12s8p1d/6s4p1d) and Al (12s8p1d/6s4p1d); the exponents for the polarization functions being $d_{\text{Si}} = 0.50$, $d_{\text{Al}} = 0.40$.

Calculations involving GeH₃, SiH₃, and AlH₂ were also performed with the 3-21+G* basis set.²⁴ As this basis set contains polarization functions on second-row atoms only, it was augmented by a single d set on carbon atoms with exponent 0.75. The same systems were computed using the LANL2DZ ECP basis set.^{21b,25}

The computations were performed on an IBM RS/6000 and a DEC-AXP-OSF/1 computer.

Results and Discussion

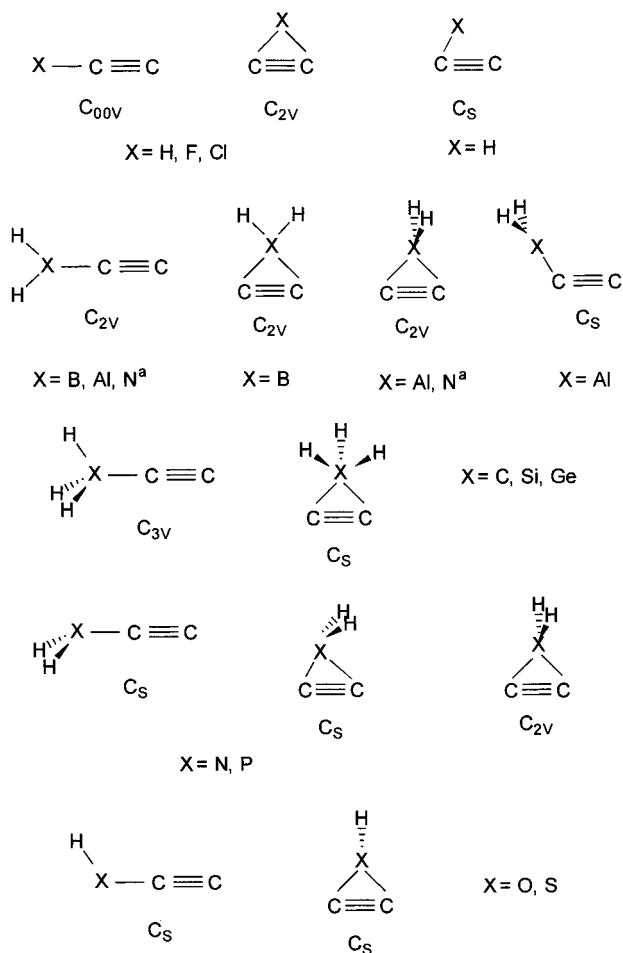
Calculations for [1,2]-anionic shifts in substituted acetylide anions were performed in order to evaluate the effect of the migrating group on the activation energy of the process (reaction 2). The selected migrating groups



were those corresponding to the groups III–VII of the periodic table for first-row (i.e., BH₂, CH₃, NH₂, OH, F) and second-row (i.e., AlH₂, SiH₃, PH₂, SH, Cl) elements, as well as for the parent compound HC≡C[−], which implies migration of the hydrogen atom. Structures are shown in Scheme 2. Results are presented in Table 1.

The parent system had been previously studied with the 6-31+G* basis set.¹⁵ In the present study the same geometry and energy for the ethynyl anion were obtained, but the transition structure found has *C_s* symmetry instead of the *C_{2v}* geometry reported therein. Actually, the *C_{2v}* structure corresponds to a minimum in the potential surface, being approximately 1 kcal/mol lower in energy than the *C_s* transition state. However, although geometries in ref 15 were optimized with the 6-31+G* basis set, harmonic vibrational frequencies were calculated with the 3-21+G basis by using geometries optimized with the latter basis set. Vibrational frequencies in this work were computed for the geometries optimized with the 6-31+G* basis. Frequency calculations on the *C_{2v}* and *C_s* RHF/6-311++G*, MP2/6-31+G*, and MP3/6-31+G*-optimized geometries evidenced that the *C_{2v}* structure is a minimum, while the *C_s* one corresponds to a transition state (Table 2). This transi-

Scheme 2. Calculated Structures for [1,2]-Shifts in Substituted Acetylide Anions



^a NO₂; i.e., O instead of H.

Table 1. Calculated Activation Energies for the Rearrangement and Differences in Zero-Point Vibrational Energies (ZPVE) for the Open and Cyclic Structures of the Substituted Acetylide Anions (kcal/mol)

group	RHF/6-31+G*	MP2/6-31+G**	MP3/6-31+G**	ΔZPVE ^a (RHF/6-31+G*)
H	24.91 40.10 ^b	26.71 40.09 ^b	24.59 38.11 ^b	3.25 3.44 ^b
BH ₂	27.89	22.46	22.38	1.12
CH ₃	46.95	45.69	43.89	1.75
NH ₂	46.64	45.80	43.55	0.46
OH	46.61	46.26	43.61	1.67
F	42.99	47.81	43.77	2.36
AlH ₂	3.29	0.80	0.54	0.30
SiH ₃	19.10 33.30 ^b	14.24 29.21 ^b	14.10 28.53 ^b	1.50 1.41 ^b
PH ₂	28.48	26.03	25.05	1.29
SH	28.32	29.90	26.99	1.28
Cl	27.57	38.59	31.79	1.90
NO ₂	45.21	45.86	43.15	1.94

^a Difference in zero-point vibrational energies between the open anion (minimum) and the transition state (ZPVE_{minimum} – ZPVE_{transition state}). ^b Li⁺ as the counterion.

tion structure was confirmed by an IRC²⁶ calculation at the RHF/6-31+G* level.

The anion and the transition state present a *C_{2v}* planar structure with BH₂ as the substituent. The alternative

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Table 2. Calculations on the Ethynyl Anion Bridged Structures

level of theory	sym group	energy (hartree)	rel energy ($C_s - C_{2v}$) (kcal/mol)	no. of imaginary frequencies
RHF/3-21+G	C_{2v}	-75.734 94	-1.40	1
	C_s^a	-75.737 17		1
RHF/6-31+G*	C_{2v}	-76.171 84	0.87	0
	C_s	-76.170 45		1
RHF/6-311++G*	C_{2v}	-76.188 06	0.88	0
	C_s	-76.186 66		1
MP2/6-31+G*	C_{2v}	-76.435 17	7.99	0
	C_s	-76.422 44		1
MP3/6-31+G*	C_{2v}	-76.434 48	1.74	0
	C_s	-76.431 71		1

^a Single point calculation of the optimized RHF/6-31+G* geometry, as this structure failed to converge with the 3-21+G basis.

cyclic geometry, with the H–B–H plane perpendicular to the C–B–C plane, has two imaginary frequencies when it is imposed to adopt this conformation; by relaxing this constraint it converges to the planar one. With AlH₂ the open anion has C_{2v} symmetry, while the transition structure presents C_s symmetry. The potential surface exhibits a minimum of C_{2v} symmetry in which the H–Al–H plane is perpendicular to the plane determined by the three heavy atoms. This structure is lower in energy than the open one. The other possible C_{2v} cyclic structure (planar) is higher in energy than the open one and has two imaginary frequencies.

Propyne anion has C_{3v} symmetry, the corresponding transition state presenting C_s symmetry. These results are in agreement with a previous study.²⁷ With SiH₃ as the substituent, the open and cyclic structures belong to the same symmetry groups as the corresponding methyl-substituted ones.

For the case of NH₂ as the substituent, the open anion as well as the cyclic transition state belong to the C_s point group. The C_{2v} structure corresponds to an intermediate on the potential surface. C_s symmetries were also found for the structures substituted by the other group V atom (PH₂), the C_{2v} bridged structure being another transition state for the migration higher in energy than the C_s one; so as the lowest transition state involves no bending of the hydrogens, this rearrangement proceeds with retention of configuration at phosphorus.

For the group VI substituents (OH, SH), the symmetry of the corresponding open anions and cyclic transition states is C_s .

Linear anions substituted by F and Cl have $C_{\infty v}$ symmetry, the transition states belonging to the C_{2v} point group.

The level of theory was increased in order to test the accuracy of the results described above. For this purpose a triple- ζ basis set augmented with diffuse functions also in hydrogen atoms (6-311++G*) was employed to calculate the ethynyl anion and those carbanions which presented lower activation energies than the parent system. Optimizations at the MP2/6-31+G* level were also carried out on these systems. Results were in very good agreement between them, ensuring the adequacy of the 6-31+G* basis set selected to perform the whole study (Table 3).

Taking into account the decrease in activation energy by changing CH₃ to SiH₃ as the substituent, it was

Table 3. Activation Energies for [1,2]-Anionic Shifts in Substituted Acetylide Anions Calculated at Higher Levels of Theory (kcal/mol)

group	RHF/ 6-311++G* ^a (Δ ZPVE) ^b	MP3/ 6-311++G*// 6-311++G*	MP2/6-31+G* ^a (Δ ZPVE) ^b	MP3/ 6-31+G*// MP2/6-31+G*
H	20.50 (3.18)	23.74	25.31 (2.18)	24.77
BH ₂	25.92 (1.22)	21.68	23.13 (0.77)	25.74
SiH ₃	17.16 (0.93)	13.84	13.43 (0.68)	13.98
AlH ₂	2.15 (0.21)	0.24	1.13 (0.12)	0.94

^a Including zero-point vibrational contribution. ^b Difference in zero-point vibrational energies between the open anion (minimum) and the transition state ($ZPVE_{\text{minimum}} - ZPVE_{\text{transition state}}$).

Table 4. Calculations of the Activation Energy for the Migration of the GeH₃ Group in the Ethynyl Anion. Comparison with Other Migrating Groups

group	MP3/ECP// ECP ^a	MP3/3-21+G*// 3-21+G*	MP3/DZ// DZ ^b	MP3/6-31+G*// 6-31+G*
SiH ₃	32.78	15.05	14.82	14.10
GeH ₃	28.97	17.63	16.18	
AlH ₂	10.96 ^c	1.35	1.19	0.54

^a LANL2DZ ECP basis set. ^b Huzinaga–Dunning double- ζ basis set augmented with polarization functions. ^c The transition state is the C_{2v} cyclic structure.

interesting to evaluate the effect of the GeH₃ group. As Ge is not defined in the 6-31+G* basis set, LANL2DZ ECP, 3-21+G*, and Huzinaga–Dunning double- ζ basis sets were used. To obtain comparable results it was necessary to employ the same basis sets to calculate other systems presumably closer in activation energy to the value expected for GeH₃; SiH₃- and AlH₂-substituted anions were chosen for this purpose. Huzinaga–Dunning, 3-21+G*, and 6-31+G* basis sets produced very similar results for each system (substituents SiH₃ and AlH₂) (Table 4). Therefore, calculations for GeH₃ would be reliable enough. In this view, migration of the germyl group presents an energy barrier comparable with that for the silyl. It is known that germanium migrates as easily as silicon in the Wright–West reaction.⁴ A theoretical study of this oxygen to carbon anionic shift is in agreement with these observations.²⁸

To evaluate the counterion effect on the barrier, calculations of the lithiated species were performed for the parent and the silicon-substituted systems (Table 1). Li⁺ was shown to raise the energy barriers by ~14 kcal/mol, as the open anions are stabilized by this amount relative to the corresponding bridged structures, where the negative charge is less localized. The same effect had been observed in an ab initio calculation of the Wright–West rearrangement for the free anion and the lithiated compound.²⁹

Rearrangement Barriers. The activation energy for the process described in reaction 2 depends on the nature of the migrating group R. In this way, most of the substituents derived from first-row elements (i.e., CH₃, NH₂, OH, and F) present almost the same activation barrier, ~44 kcal/mol (Table 1). When R = H, BH₂, PH₂, and SH, the values for the barriers are fairly close (~22–27 kcal/mol). With R = SiH₃, the activation energy decreases considerably (14.10 kcal/mol), while for R = AlH₂ it becomes almost null (0.54 kcal/mol).

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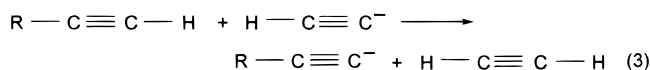
Table 5. Substituent Effect: ΔH for Isodesmic Reactions 3 and 4 (kcal/mol)^a

R	Δ_O^b	Δ_{TS}^c	$\Delta_{TS} - \Delta_O$	activation energy for the [1,2]-shift
CH ₃	5.69	25.09	19.40	43.89
F	-6.53	12.70	19.23	43.77
OH	2.85	21.92	19.07	43.61
NH ₂	7.09	26.11	19.02	43.55
Cl	-8.97	-1.72	7.25	31.79
SH	-6.27	-3.82	2.16	26.99
PH ₂	-7.02	-6.50	0.52	25.05
H	0.00	0.00	0.00	24.54
BH ₂	-12.98	-15.14	-2.42	22.38
SiH ₃	-9.66	-20.09	-10.43	14.10
AlH ₂	-10.21	-34.21	-24.00	0.54

^a MP3/6-31+G*//6-31+G* single point calculations. ^b Effect on the open anion, i.e., acidity (reaction 3). ^c Effect on the transition state (reaction 4).

To obtain an integral comprehension of the factors determining the activation barriers, the analysis of the substituent effect was divided into the examination of their influence on the open (reactant) and cyclic (transition state or intermediate) structures.

A. Effect on the Stability of the Carbanion (Acidity). The influence of each substituent on the acidity of the correspondent acetylene was evaluated according to the proton-transfer reaction 3:



The effect of R related to hydrogen on the carbanion is shown in Table 5. The total effect exerted by a particular substituent is a combination of its inductive and resonance effects.

The data in Table 5 show that NH₂, CH₃, and OH (in this order) decrease the acidity of acetylene while all the other substituents increase it. These results agree fairly well with the experimental gas-phase acidity order for those compounds whose data are available (R = F, H, CH₃),³⁰ although the compound with R = OH has been reported to be more acid than acetylene.^{30b} The BH₂ group exerted the greatest stabilization effect, as expected when considering its low-lying empty p-orbital. NBO³¹ calculations show that the occupancy of this orbital increases from 0.07 electrons in the protonated compound to 0.21 electrons in the anion. This extra π electron density in boron comes through transfer from the higher C-C π -bonding orbital, according to comparisons to the parent ethynyl anion. Continuing through the first row, the methyl group destabilized the ethynyl anion, this being the normal effect that this group

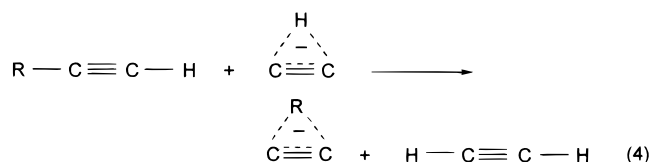
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produces on carbanions.³² The propargyl anion (HC \equiv C-CH₂⁻) has been calculated to be slightly less stable than the propynyl anion.³² The NH₂ group showed the greatest destabilization, as it is the best π -donor in the series. The OH group also produced a little destabilizing influence. For HC \equiv C-NH₂ and HC \equiv C-OH, hydrogens attached to the heteroatoms have been established to be more acidic than the acetylenic one.³² Fluorine exerted its normal stabilizing inductive effect through σ -electron withdrawal.

Second-row substituents are known to stabilize carbanions much more efficiently than their first-row counterparts, although they are in general less electronegative.³³ This is due to the greater polarizability of the second-row atoms and to the more effective negative hyperconjugation because of the availability of low-lying σ^* orbitals. The d-orbital effects do not contribute significantly, although the geometries are improved substantially upon addition of d-type orbitals which act as polarization functions.^{33,34} According to the present results, for group III elements, stabilization was brought about by electron density transfer to vacant p-orbitals; NBO calculations showed that the 4p-orbital in Al increased its population from 0.02 e⁻ to 0.09 e⁻ by deprotonation. For R = SiH₃, the anion developed 0.03 e⁻ occupancies in each σ^* Si-H and the σ^* C-Si. The acetylenic hydrogen has been observed to be more acidic than the hydrogens of the silyl group in HC \equiv C-SiH₃.³² For R = PH₂, both σ^* P-H and the σ^* C-P became populated by 0.03 e⁻. Chlorine exerted only inductive electron withdrawal. SH stabilizes anions mainly by a polarizability effect.³⁵ However, there were no wide energy differences in substituent effects within the second row.

B. Substituent Effect on the Transition State. The ability of each substituent to bridge (relative to hydrogen) was calculated by the isodesmic reaction 4:



Results related to the parent system are displayed in Table 5.

Among first-row substituents, the only stabilizing one was BH₂, due to its hypervalent nature achieved by one available empty p-orbital. The effect of this group was fairly comparable in both open and cyclic structures, leading to no appreciable changes in the activation energy of the migration process compared to the ethynyl anion. CH₃, NH₂, and OH showed similar destabilizing influence, following the same trend as with the open structure;

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this fact produced practically the same activation barrier for the corresponding rearrangements. F had a less destabilizing effect because of its greater electronegativity; nevertheless, the stabilizing effect on the linear structure and the destabilizing one on the transition state compensated each other, leading to an energy barrier equivalent to that of the other three groups of the row.

Second-row substituents stabilized the transition state to a very different extent. There were also differences in the relative stabilizations of the cyclic and open structures, and consequently, variations in the activation energies for migration were observed. Chlorine produced a slight stabilizing effect; apparently, σ - and π -effects canceled each other and considering the stabilizing influence on the linear anion, this generated a higher energy barrier than the ethynyl anion. With SH, the polarizability influence was almost the same in both structures, producing a small decrease in the activation energy for the rearrangement. This was also the case for PH₂, which showed nearly the same activation energy as the ethynyl anion.

The capability of the SiH₃ group to accomplish negative hyperconjugation produced a population of 0.06 e⁻ in each antibonding Si-H orbital and of 0.16 e⁻ in the antibonding C-C-Si three-center bond (with greatest coefficient at silicon), according to NBO analysis. This stabilization by delocalization of the electron density in the bridged structure, especially by depletion of the sp-lone pairs developed in both carbons, led to a considerably smaller barrier for the migration process. Hypervalency has been ascribed to partial ionic σ -bonding and partial π -bonding through negative hyperconjugation.³⁶ Strongly polar σ^* -orbitals has been found to be more effective electron acceptors than the extra-valence d-orbitals. However, d-orbitals are essential for a correct description of the bonding, structure, and energy of hypervalent species. They serve as additional central-atom acceptor functions and polarize the σ^* -orbitals, which improves the overlap of the central-atom valence orbitals with the ligand orbitals and decreases the ligand-ligand repulsion.^{36,37}

The additional effect of an empty low-lying π -orbital on a second-row atom drastically decreased the energy barrier for AlH₂ migration. NBO analyses revealed that, in contrast with BH₂, where the cyclic structure is described as composed by two units due to the nonexistence of any B-C bond, aluminum used its vacant orbital to build two bonding orbitals with the carbon atoms; i.e., the extra electron becomes involved in the new C-Al bond. In this case the rearrangement took place through an intermediate lower in energy than the open anion. The perpendicular orientation of the H-Al-H plane with respect to the C-Al-C plane in the C_{2v} intermediate, in sharp contrast with the planar structure adopted with BH₂, allows the formation of both Al-C bonds, Al presenting an almost sp³-hybridization. This shift proceeded with inversion in configuration at the migrating group.

Other Substituents. Calculations with more substituents were carried out to get a better understanding of the factors affecting the activation energy for the rearrangement. Substituents derived from carbon and silicon were selected.

Table 6. Calculated Activation Energies for the Rearrangement and Differences in Zero-Point Vibrational Energies (ZPVE) for the Open and Cyclic Structures of Other Substituted Acetylide Anions (kcal/mol)

group	RHF/ 6-31+G*	MP2/6-31+G** 6-31+G*	MP3/6-31+G** 6-31+G*	Δ ZPVE ^a (RHF/ 6-31+G*)
CH ₂ CH	47.17	42.78	41.96	1.65
CHO	44.19	38.34	38.38	1.37
CN	41.61	38.00	36.73	2.17
Si(CH ₃) ₃	20.60	14.95	15.24	0.88
SiF ₃	18.68	12.32	12.66	1.04
Si(SiH ₃) ₃	16.32	9.77	10.61	0.95

^a Difference in zero-point vibrational energies between the open anion (minimum) and the transition state (ZPVE_{minimum} - ZPVE_{transition state}).

Table 7. Calculations with Other Substituents. Δ H for Isodesmic Reactions 3 and 4 (kcal/mol)^a

R	Δ_0^b	Δ_{TS}^c	$\Delta_{TS} - \Delta_0$	activation energy for the [1,2]-shift
CH ₃	5.69	25.09	19.35	43.89
CH ₂ =CH	-3.67	13.75	17.42	41.96
CHO	-19.98	-6.15	13.83	38.38
CN	-29.55	-17.36	12.18	36.73
Si(CH ₃) ₃	-6.25	-15.55	-9.30	15.24
SiH ₃	-9.66	-20.10	-10.44	14.10
SiF ₃	-28.97	-40.85	-11.88	12.66
Si(SiH ₃) ₃	-16.03	-30.07	-14.04	10.50

^a MP3/6-31+G**//6-31+G* single point calculations. ^b Effect on the open anion, i.e., acidity (reaction 3). ^c Effect on the transition state (reaction 4)

A. Carbon Substituents. These calculations with unsaturated groups were done in order to evaluate the influence of resonance effects. Nevertheless, in the transition states the π -system of the substituent was perpendicular to the plane determined by the three carbon atoms of the ring, and resonance was hindered. Thus, these substituents migrate in the antarafacial manner predicted by the orbital symmetry rules. Compared to methyl, an ethenyl group stabilized the open and bridged structures to a similar extent, leading to no appreciable changes in the energy barrier. Due to the attainment of negative hyperconjugation in the hypervalent cyclic structure, inclusion of a heteroatom (R = CHO, CN) increased the stability of the transition state more than the acidity, since π^* C-X orbitals are more polarized and, hence, better acceptors than the π^* C-C orbital. In this way, NBO occupancies of the π^* C-C, π^* C-N, and π^* C-O were 0.10, 0.12, and 0.14 e⁻, respectively; this was accomplished by means of depletion of both sp-lone pairs of the acetylenic carbons, though donation to the antibonding three-center orbitals was also observed. Results are shown in Tables 6 and 7.

B. Substituents Derived from Si. The Si(CH₃)₃ group (the silicon-derived substituent more usually employed experimentally) did not produce significant changes compared with the SiH₃ group. With the Si(SiH₃)₃ group a greater stabilization of the transition state was observed. This fact suggests that a σ^* Si-Si orbital is a more efficient acceptor for negative hyperconjugation than a σ^* Si-C orbital. Substitution of hydrogens by fluorine atoms in the silyl group showed that inductive effects are not important, since the open and transition structures were relatively stabilized in an equivalent amount, although σ^* Si-F orbitals performed better in

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Table 8. Calculations for the [1,2]-Silyl Migration in the Ethenyl Anion. Activation Energies for the Rearrangement and Differences in Zero-Point Vibrational Energies (ZPVE) for the Stationary Points (kcal/mol)

SiH ₃ ^a	RHF/	MP2/6-31+G*//	MP3/6-31+G*//	ΔZPVE ^b
	6-31+G*	6-31+G*	6-31+G*	(RHF/ 6-31+G*)
anti	17.40	11.74	13.64	0.74
anti ^c	19.70	13.33	15.34 ^d	1.24
syn	51.91	48.15	48.28	1.09
anti ^e	59.18	50.51	53.48	1.92

^a Position of SiH₃ with respect to the α hydrogen in the starting anion. ^b Difference in zero-point vibrational energies between the open anion (minimum) and the transition state (ZPVE_{minimum} - ZPVE_{transition state}). ^c MP2/6-31+G* optimization. ^d MP3/6-31+G*//MP2/6-31+G*. ^e Li⁺ as the counterion.

negative hyperconjugation within the cyclic structure (0.10 e⁻ NBO occupancies). Results are displayed in Tables 6 and 7.

C. The NO₂ Group. This group provided an additional proof that inductive and resonance effects are not decisive in fulfilling the energy requirements for [1,2]-anionic migrations in acetylenic systems. NO₂ stabilized the open structure (-34.47 kcal/mol) more than the transition structure (-15.86 kcal/mol), presumably because resonance was hindered by the perpendicular position adopted by the O-N-O plane with respect to the C-N-C plane in the transition state. Negative hyperconjugation was insufficient to compensate for the strong stabilization of the minimum, producing an activation barrier of 43.15 kcal/mol, equivalent to that found with the other first-row substituents (CH₃, NH₂, OH, and F). Results are exhibited in Table 1.

Vinylic System. The ethenyl anion had shown a high activation energy for the [1,2]-hydrogen shift.¹⁵ The process presented stereoselectivity, favoring migration of the hydrogen syn with respect to the α hydrogen (activation energy 60.47 kcal/mol at the HF/6-31+G* level) over migration of the anti hydrogen (66.44 kcal/mol).

Calculations of the activation energies for the migration of a silyl group anti and syn to the α hydrogen were carried out. Results are listed in Table 8. For the anion with the silyl group syn with respect to the α hydrogen, the migration exhibited a higher activation energy than the acetylenic system, as was expected. But the process for the anion with the silyl group anti with respect to the α hydrogen generated practically the same barrier as the silylethynyl anion. Evidently, the energy barrier is determined by the orientation of the carbon chain with respect to the migrating group in the transition state, and there is no direct dependence on the hybridization. In this way, the barrier for the migration of a silyl group depends on the spatial disposition of the ligands (in this case, the hydrocarbonated moiety) in order to achieve a suitable overlapping for bonding. In the transition state for the favored migration, the Si-C and C-C bonds were shorter (1.8931 and 1.3448 Å, respectively) than the corresponding bonds in the highest transition state (2.0752 and 1.3964 Å); the shortening of the C-C bond with respect to the open structure (1.3652 Å) was especially noticeable, as an indication of an attractive bonding interaction between the electronic clouds. This result was checked by inclusion of correlation effects via MP2 optimization of the open and bridged structures, which resulted in very good agreement. NBO analysis

Table 9. Calculations of [1,2]-Shifts for the Ethyl Anion. Activation Energies for the Rearrangement and Difference in Zero-Point Vibrational Energies (ZPVE) for the Stationary Points (kcal/mol)

group	RHF/	MP2/6-31+G*//	MP3/6-31+G*//	ΔZPVE ^a
	6-31+G*	6-31+G*	6-31+G*	(RHF/ 6-31+G*)
SiH ₃	4.16	3.40	3.12	0.86
SiH ₃ ^b	38.33	30.78	32.47	1.64
CH ₃	109.89	87.70	93.99	6.14
CH ₂ CH	10.50	1.42	4.52	2.71

^a Difference in zero-point vibrational energies between the open anion (minimum) and the transition state (ZPVE_{minimum} - ZPVE_{transition state}). ^b Li⁺ as the counterion.

showed that in the lowest transition state silicon forms one two-electron bond with each carbon atom. Nevertheless, the total d-orbital occupancy of silicon is only 0.06 e⁻, in accordance with the criterion that d-orbitals act primarily not as valence but as polarization functions that enhance bonding to the central-atom in hypervalent compounds.³⁶ In the highest transition, one three-center C-C-Si bond is formed, while the π-bond between the carbon atoms has broken.

Isomerization of the (*Z*)- and (*E*)-silylethylene anions proceeded through a potential energy surface where the α hydrogen moves in the Si-C-C plane to invert the anionic center, which becomes linear in the transition state. The activation energy for the isomerization process at the HF/6-31+G* level was 33.85 kcal/mol. This value is very close to the one calculated in ref 15 of 34.18 kcal/mol for inversion at the anionic carbon in the ethenyl anion; other similar values have been found theoretically and experimentally.³² Due to the height of this barrier, [1,2]-migration of silicon in ethenyl anions would be expected to occur with high stereoselectivity.

The counterion influence on the lowest barrier was evaluated by calculation of the lithiated structures. The lithium cation increased the activation energy by ~40 kcal/mol.

Aliphatic System. In view of the interesting results obtained with the acetylenic and vinylic compounds, calculations for the silyl migration in the saturated system were performed (Table 9). The anionic center was pyramidal in the minimum, with the lone pair anti-periplanar to the β C-Si bond. In this case the activation energy was even lower (3.12 kcal/mol), in sharp contrast with the high energy barrier found for the hydrogen shift in the ethyl anion in ref 15. This provided an additional proof that the barrier does not depend on the hybridization of the hydrocarbonated system but on its orbital orientation with respect to the migrating group and the capability of the latter to achieve hypervalent bonding. As well as for the syn migration in the vinylic anion, silicon formed one two-electron bond with each carbon atom in the transition state. Total occupancies of d-orbitals were only 0.05 e⁻. Calculation of the lithiated structures indicated that Li⁺ raises the energy barrier by ~30 kcal/mol.

Obviously, strain effects should be important for the formation of the bridged structure and this fact was reflected in the activation energies for silyl as the migrating group. In this way, the barriers 14.1 kcal/mol for the ethynyl, 13.6 kcal/mol for the ethenyl (syn migration), and 3.12 kcal/mol for the ethyl anion followed the expected order according to the strain of the carbonated system. Enhancement of the overlap for bonding

in the transition states is evidenced by formation of one three-center C–C–Si bond in the ethynyl and (*E*)-silylethylene anions and two Si–C bonds in (*Z*)-silylethylene and ethyl anions. Population of antibonding molecular orbitals (Si–H, C–C–Si, and C–Si) by means of negative hyperconjugation also increased in this order.

As previously mentioned, trimethylsilyl and vinyl groups undergo [1,2]-anionic shifts between carbon atoms, while alkyl groups have not been observed to migrate. As a test of the theoretical results in this paper, the [1,2]-migration of the methyl group in the *n*-propyl anion was calculated (Table 9). The open anion was pyramidal at the anionic carbon with the lone pair antiperiplanar to the β C–C bond (C_s symmetry). The transition state exhibited C_s symmetry, as for SiH_3 , but the energy barrier was considerably higher: 93.99 kcal/mol at the MP3/6-31+G**/6-31+G* level. At the Hartree–Fock level, the structure presented two imaginary frequencies and the minor of them was eliminated by optimization at the MP2/6-31+G* level. NBO calculations revealed that the methyl links to the other two carbons by two bonds, which delocalize through electron density promotion into the 3p-orbitals of the methylenes. This high-energy electronic distribution (0.12 e^- in each of both 3p-orbitals) would explain the unstability of the structure. This result agrees fairly well with Zimmerman and Zweig considerations concerning the unfeasibility of [1,2]-alkyl anionic shifts.^{9a} However, the rearrangement proceeded in a suprafacial–suprafacial manner; the suprafacial–antarafacial process (with inversion of configuration at the methyl group) allowed by the Woodward and Hoffmann orbital symmetry rules resulted in loss of a methyl anion to give ethylene. Both processes are diagrammed in Scheme 1.

Migration of an unsaturated group was calculated by means of the rearrangement of the 1-butene anion (anionic center at C_4) (Table 9). The minimum structure presented C_s symmetry with the lone pair antiperiplanar to the β C–C bond. The vinyl group migrated antarafacially, but in the transition state the double bond was broken due to rotation of the terminal carbon, which develops a π -lone pair. Optimization at the MP2 level was necessary to remove one spurious imaginary frequency. According to NBO calculations, two bonds are formed with both carbons of the alkylic moiety, the lone pair being perpendicular to the three-membered ring. Thus, most of the negative charge localizes in the terminal carbon. This factor determines the lowering of the barrier for the rearrangement, as has been pointed out elsewhere,^{9b,6b} which becomes 4.52 kcal/mol at the MP3/6-31+G**/6-31+G* level.

In this way, the present calculations yield activation energies that are in accordance with known experimental data. A silicon atom as well as an unsaturated group presented low energy barriers for migration, these rearrangements being known experimentally. On the other hand, the extremely high barrier observed for the methyl shift properly accounts for the lack of evidence of carbanionic alkyl migrations in the literature.

Effect of the Counterion. Comparison of the calculations for the silyl migration in the ethynyl, ethenyl (syn migration), and ethyl anions with lithium as the counterion led to the following observations: for the open anions (minima), stabilization by Li^+ increases with decreasing s-character of the anionic center; i.e., the ethyl

anion stabilizes more than the ethenyl and the ethynyl more than the ethynyl.

The rearrangement barriers followed the stabilization order of the lithiated transition states. Therefore, the cyclic structure derived from the ethynyl anion stabilized the most and produced the minor activation energy, while the one derived from ethenyl generated the highest barrier. These results may be rationalized according to repulsions between lithium and the hydrogen atoms of the hydrocarbonated moiety: ethynyl, no Li–H repulsions; ethyl, Li–H of 2.18 and 2.22 Å; ethenyl, Li–H of 1.83 Å. The Li–C distance was almost equal for the three systems (~ 2.0 Å).

Conclusions

The migratory ability of a given atom or group of atoms for [1,2]-anionic shifts lies on its capability to attain hypervalent bonding. This process is achieved by means of negative hyperconjugation, which produces a substantial stabilization of the transition state for migration. As valence empty p-orbitals and low-lying π^* - or σ^* -orbitals are the best acceptors, their availability is crucial for the rearrangement to take place. On the other hand, population of extravalence d-orbitals is negligible. Polarizability of the migrating atom is also important. As a result of these requirements, substituents derived from second-row elements (especially from groups III and IV) are better migrating groups than their first-row counterparts.

The energy requirements for [1,2]-anionic shifts depend mostly on the ability of the migrating atom to form a stable hypervalent structure. Spatial requirements should be satisfied in order to get a geometric disposition for optimum positive orbital overlapping. Therefore, the hybridization of the carbanionic center influences the strain of the cyclic transition state and determines the height of the energy barrier, as it was demonstrated by the silyl shift in the unsaturated and saturated anions.

The lithium cation as the counterion increases the computed activation energies for migration. The increase is ascribed to the fact that the transition states are less stabilized by Li^+ than the correspondent minima due to the negative charge delocalization. The increment of the energy barrier seems to be related to repulsions between lithium and hydrogen atoms as it is proportional to the Li–H distance in the transition state.

Acidity of the acetylene derivatives is dominated mainly by normal inductive and resonance effects. The presence of low-lying empty π -orbitals or low σ^* -orbitals for the attainment of negative hyperconjugation is also important.

These theoretical results are in very good agreement with known experimental data concerning [1,2]-anionic shifts between carbon atoms, which supports the validity of the methodology employed for this study. Although the solvent effect has not been taken into account, the calculated activation energies may serve as a guide concerning the migratory ability of the groups. In view of this, it is deduced that some so far unknown rearrangements could be found experimentally. Among them, the anionic migration of germanium could be observed, and the same applies for aluminum, with which the carbanion would present a cyclic structure. Silicon shifts, which until now have been observed only in

saturated carbanions, would be expected to take place also in unsaturated systems.

Acknowledgment. The author thanks the Technion-Israel Institute of Technology for a postdoctoral fellowship, as well as for the availability of computational resources, and gratefully acknowledges Professor Yitzhak Apeloig for helpful discussions.

Supporting Information Available: Tables with total and zero point energies, and geometrical data for all the optimized structures in the form of tables and figures (13 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.

JO972179A