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Counterion Effects on the Wright–West Anionic Migration Reaction. An ab Initio Theoretical Study

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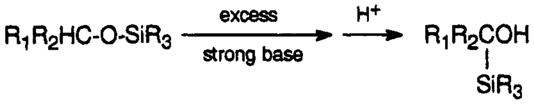
The [1,2] silyl migration in the $(H_2COSiH_3)Li$ model system has been studied, following a first study on the related free anion, to investigate the effects of the lithium counterion on the reaction mechanism. As was the case in the absence of lithium, the nondissociative rearrangement takes place in two steps, passing through a cyclic intermediate in which silicon is pentacoordinate. Lithium stabilizes the intermediate less than the carbanionic "reactant" and the oxyanionic "product" and raises as a consequence the energy barrier, but has a small effect on the reaction exothermicity. As an alternative pathway, the initial lithiated carbanion can undergo heterolytic dissociation of the O–Si bond without complete separation of the H_2CO and SiH_3^- fragments, which are held together by the interaction with Li^+: an electrostatic complex is then formed between formaldehyde and silyllithium. From this intermediate the same product of the nondissociative [1,2] shift could be easily obtained through a reassociation step. However, the energy barrier for the first dissociative step is much higher than that for the direct [1,2] migration, which is then the preferred pathway. Comparison of these results with those obtained for the free anions leads to the conclusion that the Wright–West migration takes place in a two-step process where the C–Si bond is formed before the O–Si bond is cleaved, and not vice versa.

Introduction

The Wright–West rearrangement[1] is the transformation of a silyl ether into its isomeric alcohol, taking place in the presence of excess strong base.[2] In this reaction a trialkylsilyl group[3] migrates from oxygen to carbon (Scheme 1): it is therefore the silicon analogue of the well-known Wittig rearrangement,[4] where an alkyl, aryl, or allyl group migrates on the same underlying skeleton.

Scheme 1



$$R_1R_2HC\text{-}O\text{-}SiR_3 \xrightarrow[\text{strong base}]{\text{excess}} \xrightarrow{H^+} R_1R_2\underset{\displaystyle SiR_3}{\underset{|}{C}}OH$$

The theoretical study of this reaction was recently undertaken[5] by studying the simple H_2COSiH_3 free anion and, for comparative purposes with the Wittig rearrangement, the analogous H_2COCH_3 anion. In paper 1 the extreme situation in which the interaction with the cation is not present was studied in order to examine in the simplest way various aspects of the nature of these migrations. The competition of the [1,2] shift with a dissociative process was considered, in order to assess if a direct migration can be considered a realistic pathway from the carbanionic "reactant" to the oxyanionic "product", and the resulting different behavior of the silicon and carbon systems was discussed in terms of electron distribution and bonding. Here, the silicon rearrangement is reexamined in the presence of a lithium counterion that can be directly bound either to carbon or to oxygen (or both) during the migration process. Therefore, this study provides another extreme picture of the evolution of the anionic H_2COSiH_3 model system, allowing discussion of the possible role of the counterion in affecting the reaction mechanism.

The gas-phase energy profile for the direct migration of the silyl group has to be defined, in order to establish if the cyclic pentacoordinated-silicon intermediate, which was the more important feature of the free-anion rearrangement, is still found in the presence of the counterion; in that case, the extent of the stabilization or destabilization operated by lithium on intermediate and transition structures with respect to the "reactant" (or "product") is to be determined. Then, a dissociation–reassociation process is studied, involving the cleavage of the Si–O bond and the subsequent formation of the C–Si bond; in paper 1 such a process was estimated to be unfavorable with respect to the direct [1,2] shift.

Method

The study of the rearrangement reaction was performed by determining on the energy hypersurface the critical points relevant to stable and transition structures. This was ac-

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(1) Wright, A.; West, R. *J. Am. Chem. Soc.* **1974**, *96*, 3214–3221 and 3227–3232.

(2) When the base is present in catalytic amounts, the reverse migration takes place, giving alkoxysilanes from α-silyl carbinols (anti-Wittig or Brook rearrangement): Brook, A. G.; Legrow, G. E.; MacRae, D. M. *Can. J. Chem.* **1967**, *45*, 239–253. Brook, A. G.; Warner, C. M.; Limburg, W. W. *Can. J. Chem.* **1967**, *45*, 1231–1246. Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77–84. For a recent experimental paper dealing with the Brook rearrangement (in which kinetic and stereochemical results are discussed) see: Reich, H. J.; Holtan, R. C.; Bolm, C. *J. Am. Chem. Soc.* **1990**, *112*, 5609–5617.

(3) It also takes place on other substrates; see, for instance: Lautens, M.; Delanghe, P. H. M.; Goh, J. B.; Zhang, C. H. *J. Org. Chem.* **1992**, *57*, 3270–3272. Danheiser, R. L.; Fink, D. M.; Okano, K.; Tsai, Y.-M.; Szczepanski, S. W. *J. Org. Chem.* **1985**, *50*, 5393–5396. Ireland, R. E.; Varney, M. D. *J. Am. Chem. Soc.* **1984**, *106*, 3668–3670. Cohen, T.; Matz, J. R. *J. Am. Chem. Soc.* **1980**, *102*, 6900–6902.

(4) Wittig, G.; Lohmann, L. *Ann.* **1942**, *550*, 260–268. Wittig, G. *Angew. Chem.* **1954**, *66*, 10–17.

(5) Antoniotti, P.; Tonachini, G. *J. Org. Chem.* **1993**, *58*, 3622–3632 (referred to as paper 1).

0022-3263/94/1959-3952$04.50/0

complished by way of complete gradient optimization[6] of the geometrical parameters at the Hartree−Fock level of theory using the split-valence shell $3\text{-}21{+}G^{(*)}$ basis set[7] (diffuse sp functions are centered on all non-hydrogen atoms and d polarization functions only on silicon; diffuse functions on lithium are omitted). In one case (a transition structure for dissociation) the results obtained at the monodeterminantal level of theory were checked by redetermining the optimum structure by MC-SCF calculations (further details will be provided in the following section). The critical points were characterized as minima or first-order saddle points through diagonalization of the analytically calculated Hessian matrix (vibrational frequencies calculation). In the figures of the following section the reported interatomic distances are in angstroms and angles in degrees (dihedral angles in parentheses). The corresponding geometries were used for recomputing the relative energies at a higher theoretical level, introducing correlation effects through perturbative MP3 computations,[8a] in conjunction with the 6-31+G(d) basis set[9] (containing both diffuse sp functions and d polarization functions on all non-hydrogen atoms). The height of the two more important energy barriers was recomputed at the MP4 level of theory[8a] and through coupled cluster calculations (at the CCSD(T) level),[8b] using the same basis set. The GAUSSIAN88 and GAUSSIAN92 systems of programs[10] were used throughout on a VAX Station 3200 + 3150 cluster and on an IBM RISC/6000−550 at the Istituto di Chimica Organica.

Results and Discussion

The Nondissociative Pathway. The gas-phase energy profile for a direct migration of the silyl group from oxygen to carbon has first been defined. The present calculations confirm the free-anion results of paper 1, in that the nondissociative pathway for the silyl group transposition is still described as a two-step migration passing through a stable cyclic intermediate. In the more stable geometry of the "reactant" (siloxymethyl)lithium (Figure 1a) the cation is involved in a bridging interaction with both carbon and oxygen; the C−Li bond is therefore antiperiplanar with respect to the O−Si bond; in regard to the methylenic hydrogens, this conformation is the same found for the free anion (**1a**, paper 1). This conformation could be labeled for convenience as "W", from the position of silicon relative to the two methylenic hydrogens in a Newman projection. A transition structure (Figure 1b), in which lithium leaves oxygen through a rotation of the $CLiH_2$ group, puts it into relation with a second stable structure (Figure 1c), in which lithium

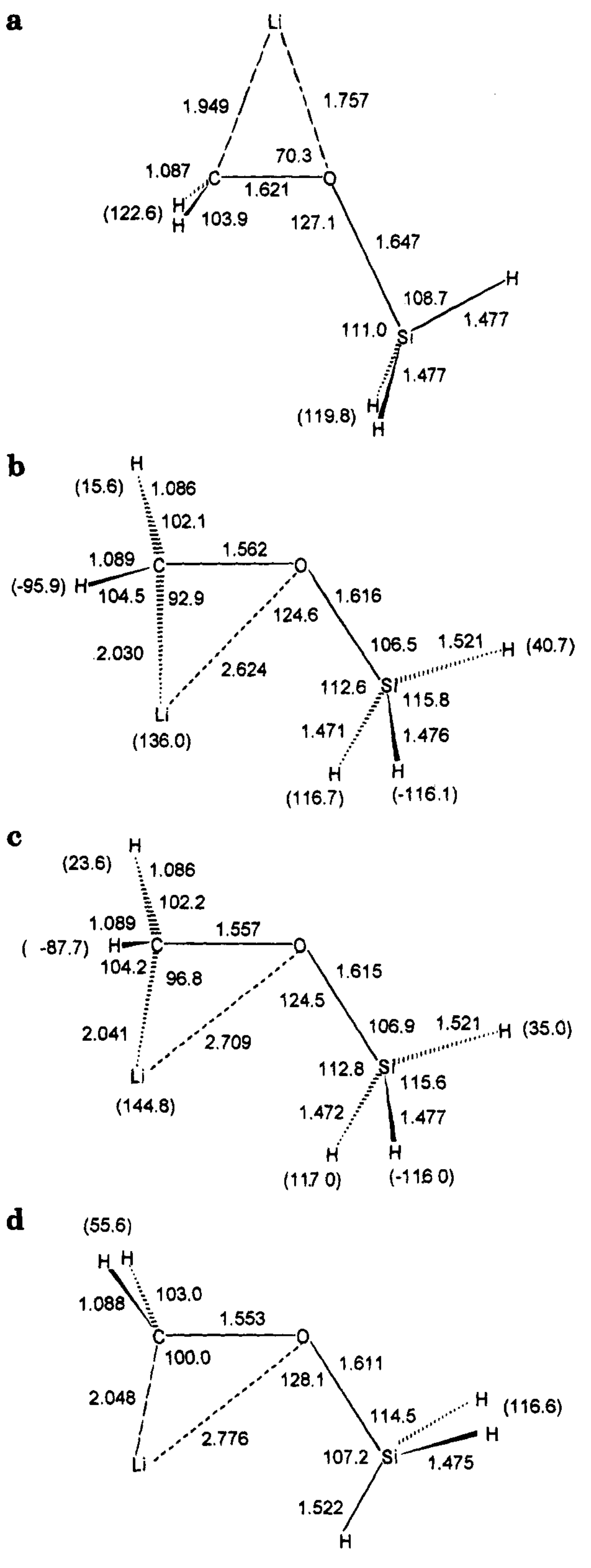

Figure 1. (Siloxymethyl)lithium: (a) the more stable "W" minimum (C_s), with Li and Si in an antiperiplanar conformation; (b) rotational transition structure (C_1) connecting **1a** to **1c**; (c) secondary minimum (C_1); (d) transition structure connecting two equivalent **1c** minima (C_s, synperiplanar Li and Si). Dihedral angles (reported in parentheses) other than HCOLi and HSiOH refer to a dummy center bound to oxygen, perpendicular to the CO bond, and antiperiplanar to silicon.

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Table 1. Total[a] and Relative[b] Energies of the Critical Points

		MP3/6-31+G(d)[c]		RHF/3-21+G(*)	
structure (Li to Si relation)		*E*	Δ*E*	*E*	Δ*E*
"W" reactant (*anti*)	**1a**	−412.422 317	0.0	−409.939 251	0.0
conform TS (*gauche*)	**1b**	−412.408 321	8.8	−409.912 965	16.5
reactant (*gauche*)	**1c**	−412.408 253	8.8	−409.912 980	16.5
conform TS (*syn*)	**1d**	−412.406 712	9.8	−409.912 747	16.6
TS (from **1a** to **2c**, CH_2 inv.)	**2a**	−412.395 596	16.8	−409.903 186	22.6
TS (from **1a** to **2c**, CH_2 rot.)	**2b**	−412.381 994	25.3	−409.894 273	28.2
"Y" reactant (*anti*)	**2c**	−412.396 757	16.0	−409.904 374	21.9
TS for ring closure	**3a**	−412.398 486	14.9	−409.903 325	22.5
cyclic intermediate	**3b**	−412.416 541	3.6	−409.915 970	14.6
TS	**4a**	−412.416 308	3.8	−409.912 850	16.6
product	**4b**	−412.442 828	−12.9	−409.941 495	−1.4
dissociation TS	**5a**	−412.347 471	46.9	−409.806 279	83.4
dissociation TS	**5b**	−412.334 551	55.1	−409.785 955	96.2
complex	**5c**	−412.403 335	11.9	−409.881 757	36.1
reassociation TS	**5d**	−412.395 211	17.0	−409.865 055	46.6

[a] Hartrees. [b] kcal mol^{-1}. [c] Computed at the RHF/3-21+G(*) geometries of the critical points.

is gauche to silicon; this secondary minimum is located at higher energy (Table 1). In the transition vector of **1b** the main components reflect the mentioned rotation (the coefficients are 0.55 for the lithium dihedral angle and 0.48 and 0.49 for the two hydrogen dihedral angles), accompanied by an opening (or closure) of the LiCO angle (0.34 coefficient) and a rotation of the silyl group (0.30 coefficient). In **1c** the stabilizing double interaction of lithium with both carbon and oxygen present in **1a** is no longer possible (indeed, this interaction is almost completely lost already in **1b**). Both **1b** and **1c** structures have C_1 symmetry and have counterparts equivalent to them by symmetry, which are obtainable by reflection through the COSi plane. Therefore, the two equivalent secondary minima **1c** so defined are separated by a transition structure of C_s symmetry, corresponding to a synperiplanar arrangement of the Li and Si atoms (Figure 1d). Although the gauche minimum **1c** exists on the computed RHF energy hypersurface, it appears to be quite shallow, separated from the more stable minimum **1a** by an evanescent barrier (see Table 1).

Another stable conformation of the lithiated carbanion is reachable from **1a** in two different ways: either through a transition structure involving methylene inversion (Figure 2a), or through a transition structure in which the methylenic hydrogens rotate (Figure 2b). The motion of the two hydrogens is accompanied in both cases by some shift of lithium toward oxygen. Both pathways lead to the same energy minimum (Figure 2c), which corresponds to a conformation of the two methylenic hydrogens with respect to silicon, such that this stable structure could be labeled as "Y" (considering the Newman projection); lithium is anti to silicon as in **1a**. The LiC bond is longer than in **1a** (by 0.27 Å), and the LiOC angle is larger by almost 15°, but lithium is still in a bridging position between carbon and oxygen. The COSi angle changes significantly with respect to **1a**, being smaller by 22°. Also, this third energy minimum is less stable than **1a** (Table 1). It can be recalled that in paper 1 a Y conformation of the free carbanion was not stable with respect to ring closure, which occurred through C—Si bond formation without any energy barrier from any guessed Y geometry. Indeed, the transition structures **2a** and **2b** are in some way reminiscent of the two transition structures with CH_2 inversion or rotation which were found in the case of the free anion. These structures (paper 1, **1b** and **-c**), although potentially connecting the initial carbanion W conformation to a Y conformation, were actually leading to direct ring closure.

In Figure 3a the structure corresponding to a first-order saddle point for the migration process is shown. As silicon gets closer to the carbon atom, lithium is forced to abandon carbon and moves around oxygen by rotating in the same direction as silicon (clockwise in Figure 3a), while fully keeping its interaction with oxygen. The transition vector is dominated by the motion of the silyl group almost parallel to the CO bond (−0.68 coefficient for the COSi angle), coupled with the change in the LiOC angle (0.43 coefficient); smaller contributions come from the HSiO angles and relevant dihedral angles. The geometrical parameters of **3a**, and the nature of the relevant transition vector, suggest that this transition structure is more likely to represent a connection of the cyclic intermediate with the secondary minimum **2c**, rather than a direct connection with the more stable structure **1a**. The **2c** to **3a** energy barrier is only 1.6 kcal mol^{-1} at the RHF level. However, the usual procedure of performing single-point higher-level energy evaluations on the structures optimized at some lower level of theory (which effects in this case an arbitrary cut on the MP3 energy hypersurface) yields here a small negative MP3 energy difference between **3a** and **2c** (−1 kcal mol^{-1}, Table 1). Nevertheless, we end up with the information that ring closure from the more stable structure of the lithiated carbanion (**1a**) would require overcoming an overall energy barrier of ca. 15 kcal mol^{-1}, given the energy difference between the more stable minimum **1a** and the secondary minimum **2c**.

The transition structure **3a** leads to a pentacoordinate-silicon cyclic intermediate, corresponding to a well-defined minimum on the energy hypersurface (Figure 3b). Therefore, an essential feature of the silicon rearrangement, as determined in paper 1 for the free anion model system, is kept. In **3b** lithium has moved further and is now almost collinear with the C—O axis, while silicon is closer to carbon; the other geometrical parameters have not changed very much from their values in the transition structure. In this minimum the conformation of the silyl group with respect to the CO bond is the same as in the lithiated carbanion **1a** and in the transition structure **3a**.

The ring-closure process can be seen as an electrophilic substitution at carbon, where silicon displaces lithium,

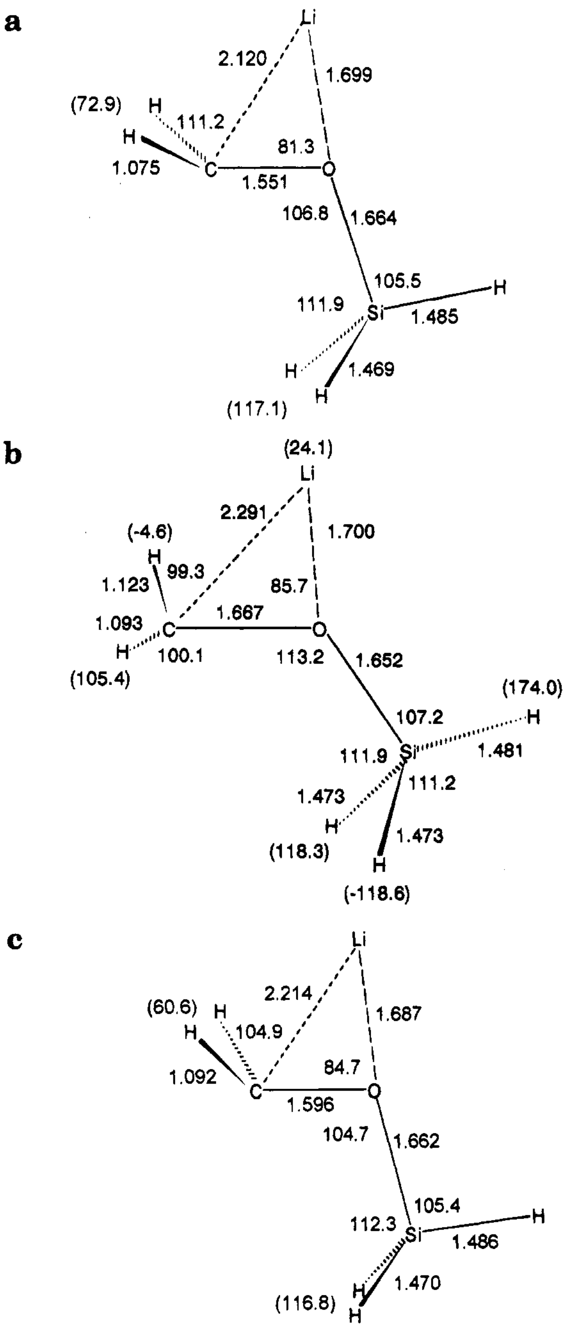

Figure 2. (Siloxymethyl)lithium: (a) CH_2-inversion transition structure connecting the more stable minimum **1a** to **2c**; (b) rotational transition structure connecting **1a** to **2c**; (c) "Y" minimum (C_s), with antiperiplanar Li and Si. Dihedral angles are reported as in Figure 1, with the exception of HSiOC in (b), relevant to the rightmost hydrogen atom.

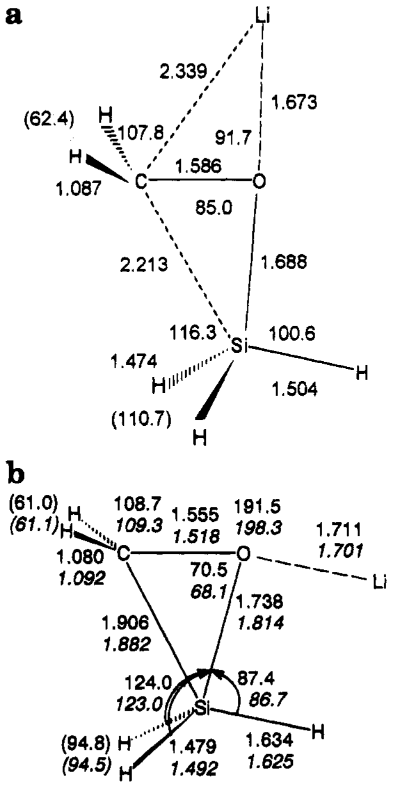

Figure 3. Nondissociative silyl migration: (a) first transition structure; (b) the cyclic minimum; MP2/6-31+G(d) results in italic (see text). Dihedral angles (reported in parentheses) refer for the methylenic hydrogens to a dummy center bound to oxygen, perpendicular to the CO bond, and antiperiplanar to silicon; for the silyl group the dihedral angles are defined as HSiOH.

as well as a nucleophilic displacement at silicon, with carbon as the incoming nucleophile and OLi as the leaving group. While in the free anion transition structure (**1b**, paper 1) the H_2CO group is almost planar and the COSi angle still very open (the geometry is closer to the open-chain W carbanion geometry than to the cyclic intermediate), in the transition structure **3a** the motion of the silyl group (expressed for instance in terms of the COSi angle) has proceeded to a significant extent. This first part of the reaction path features an important difference with respect to its counterpart in paper 1, namely the endothermicity of the formation of the cyclic intermediate (Table 1). This is consistent with the geometrical changes just discussed: from this point of view, the transition structure is closer to the intermediate than to the reactant, in accord with the Hammond postulate (see the RHF energies; the endothermicity is nevertheless greatly reduced in the MP3 computations). Lithium thus stabilizes the initial carbanion more than the intermediate. This different stabilizing interaction is consistent with the electron distribution discussed in paper 1 on the basis of dipole moments and NAO charges.[11] In the free carbanion the charge was more localized (see Table 2 in paper 1), and consequently this structure is here more inclined to a significant ionic interaction with the counterion; in the free anion cyclic intermediate, on the contrary, some redistribution of the electron density toward the silyl group had taken place and the charge was less localized (compare, for instance, the position of Li^+ in **3b** with the dipole moment reported in Chart II of paper 1 for the cyclic intermediate A). Concurrently, the energy of the HOMO was higher in the carbanion than in the intermediate: the empty 2s orbital of Li^+ can then interact to a greater extent with the HOMO of the former. The different stabilization achieved in the two cases can be thought of as being at the origin of the energy difference between **1a** and **3b**; on the other hand, the partial loss of the mentioned stabilizing interaction, consequent to methylene inversion, gives rise to the energy difference between **1a** and **2c**.

As recalled above, in paper 1 two possible migration pathways connecting the initial carbanion to a cyclic intermediate were discussed: an inversion transition

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[11] Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735–746.

structure was found to characterize one of the pathways, while the other pathway went through a CH_2-rotational transition structure. The stereochemical outcome of a reaction involving a negative carbon bearing two different groups would of course depend on which pathway is preferred. While in the case of a free anion the rotational transition structure was related to the lowest energy barrier, here the "CH_2-inversion with Si-migration" pathway **1a**–**2a**–**2c**–**3a**–**3b** seems to be the best possibility offered to a lithiated system (Table 1). This in turn suggests that the stereochemistry of the migration process could depend to some extent on the degree of cation–anion association.

A second conformation of the cyclic minimum, corresponding to **2b** of paper 1, with the silyl group rotated 180° with respect to its position in **3b**, was not found. Any attempt to optimize such a structure resulted in breaking of the Si—O bond and ring opening, and the system evolved downhill toward the lithium silylmethoxide product. The reason may be the following: OLi is a better leaving group than O^-; in minimum **3b** it occupies an almost equatorial position around the pentacoordinated silicon, but when it is put in an almost axial position (as is done when attempting to optimize the other conformation) it plainly leaves,[12] without any energy barrier. (In a backward migration, from **3b** to **1a**, the situation would be different: although carbon occupies an almost axial position in **3b**, which is favorable for a leaving group, lithium is bound to oxygen, and thus the leaving group would not be CLi but C^-: this process is estimated here to require more than 10 kcal mol^{-1}). A second transition structure (Figure 4a) separates the cyclic minimum **3b** from the product lithium silylmethoxide (Figure 4b). The transition vector in **4a** is dominated by the rotation of the SiH_3 group (the relevant dihedral angle coefficient is 0.68) and the translation of the silicon atom approximately parallel to the CO bond (0.54 coefficient, see Figure 4a). The second energy barrier, significantly lower than the first one, is only 0.2 kcal mol^{-1} at the MP3 level (in the case of the ring opening in the free anion this step was slightly more difficult, requiring ca. 3.5 kcal mol^{-1}). The result of these single-point energy calculations could cast some doubts on the existence, at a correlated level, of the energy minimum corresponding to the cyclic intermediate. Because of the importance of this qualitative feature of the energy hypersurface, the persistence of a stable ring structure was checked by MP2/6-31+G(d) optimizations. A first energy minimization was carried out on **3b** and smoothly converged to an energy minimum. Then the search for a first-order saddle point for ring opening was carried out, starting from the guess RHF geometry of **4a**. This optimization also proceeded regularly (with a constant Hessian index of 1) and allowed us to assess the energy barrier for ring opening, which was indeed confirmed to be very low at this level of theory: 0.4 kcal/mol.[13] The optimum MP2 parameters are reported in Figures 3b and 4a, respectively. The more significant differences with respect to the RHF/3-21+G(*) results are relevant to the CO and SiO distances and to the LiOC angle.

The exothermicity of the overall [1,2] shift is slightly reduced by the presence of the counterion (−14.7 kcal mol^{-1} in the free anion). Thus, two main results have been obtained for the direct [1,2] migration pathway in a situation of tight anion–cation interaction: (i) a cyclic intermediate with pentacoordinate silicon, found for the free anion, is still involved, and (ii) the overall migration process is almost as exothermic as in the free anion system, but the energy barrier is significantly raised.

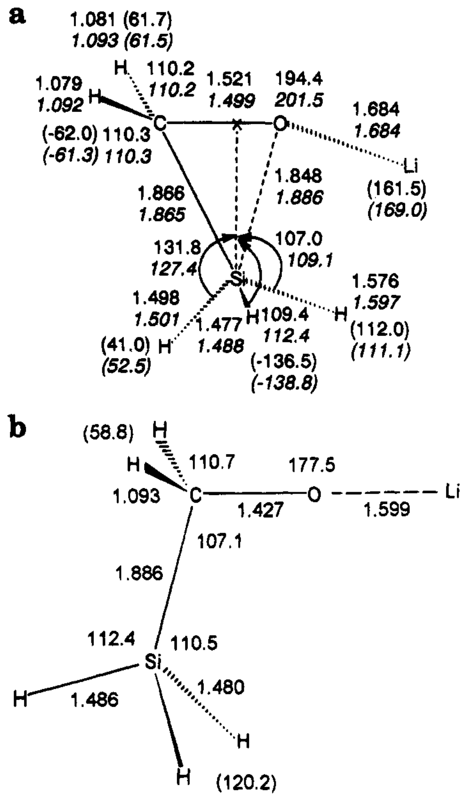

Figure 4. Nondissociative silyl migration: (a) second transition structure; MP2/6-31+G(d) results in italic (see text); (b) the lithium silylmethoxide minimum. Dihedral angles (reported in parentheses) are defined for the methylenic hydrogens as in Figure 3. For the silyl group these are in (a): for the leftmost hydrogen H′, H′SiXC (where X is a point defined by the projection of Si onto the CO bond); for the two remaining hydrogens, two HSiXH′ angles. In (b) the silyl group dihedral angles are HSiCH.

The Dissociative Process. A dissociation of the reacting system in two fragments, taking place by cleavage of the O—Si bond, followed by reassociation through formation of a new C—Si bond, would give the same product (**4b**) obtained through the nondissociative migration discussed above, in which the C—Si bond was formed before the cleavage of the O—Si bond. The heterolytic dissociation limit (corresponding to fragmentation into formaldehyde and silyllithium) is the lowest one: 31 kcal mol^{-1} above **1a**), while the homolytic (formaldehyde radical anion associated to a lithium cation and silyl radical) is at higher energy (60 kcal mol^{-1} above **1a**). However the reacting system could follow a dissociation–reassociation pathway without necessarily attaining the dissociation limit. This possibility is suggested by the fact that the H_2CO and $LiSiH_3$ moieties can most likely be held together in an electrostatic complex by a simultaneous stabilizing interaction of oxygen and silicon with lithium. From this energy minimum, reassociation of the two molecules could then take place to give the product. Therefore, a process taking place through the cleavage of the O—Si bond and without attainment of complete separation of the resulting fragments was explored, and

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[12] Compare: Deiters, J. A.; Holmes, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 1686–1692, 1692–1696. Deiters, J. A.; Holmes, R. R.; Holmes, M. H. *J. Am. Chem. Soc.* **1988**, *110*, 7672–7681.

[13] The MP2/6-31+G(d) energies of **3b** and **4a** are −412.427 355 H and −412.426 687 H, respectively.

two transition structures for the O–Si bond cleavage were determined. In the first one, which can be thought of as related to the lithiated carbanion in which lithium is *anti* to silicon (W or Y conformations), the cation participates in the dissociation process by completely leaving the carbon atom and migrating to a position in which it interacts with both oxygen and silicon (Figure 5a). The transition vector has three larger components, describing an opening of the COLi and H′SiO angles (coefficients 0.48 and 0.46, respectively; with H′ we denote the H atom lying in the COSi plane) as the SiO distance (0.59) grows larger; smaller components describe the contraction of the CO bond, the flattening of the H_2-CO group, the opening of the COSi angle, and closure of the two HSiO angles (−0.15 both). Dissociation through this pathway appears to be difficult (Table 1).

Dissociation from minimum **1c** could be interesting only if it were significantly easier than the one just discussed. The optimized geometry of the transition structure for dissociation from the secondary minimum **1c** is shown in Figure 5b. The transition vector has two dominant components: the SiO distance (0.73 coefficient) and the H′SiO angle (0.41 coefficient). The MP3 estimate of the dissociation barrier is again high, and the energy difference with respect to **1c** is comparable to the **1a**–**5a** barrier. The overall **1a**–**1c**–**5b** process is thus unfavorable. Finally, in Figure 5c the optimized structure of a rather stable electrostatic complex between formaldehyde and silyllithium is shown: both transition structures **5a** and **5b** can be thought of as connecting the lithiated carbanion, in one of its conformations, with this energy minimum.

The results obtained at the Hartree–Fock level of theory on the heterolytic cleavage taking place through structure **5a** were checked by MC-SCF calculations.[14] The optimum geometrical parameters of the transition structure were then redetermined (Figure 5a): the larger differences involve the COLi angle (−6°) and the SiOC angle (+5°); the SiO distance is also shorter by 0.16 Å. Considering all the geometrical changes which take place in the process, this transition structure is described as "earlier" with respect to the geometrical description obtained at the SCF level; however, from a qualitative point of view, the dissociation process is described as taking place through the same kind of geometrical changes. With the same active space, an MCSCF energy computation was carried out on the lithiated carbanion **1a**, using the RHF geometry, in order to get a rough estimate of the overall energy barrier for dissociation at this level of theory: the calculated energy difference is 51 kcal mol^{-1}.

In order to get a complete picture of the dissociation–reassociation pathway, the transition structure for reassociation has also been determined. From the electrostatic complex **5c** the "product" **4b** can be obtained by passing through a transition structure in which the Li–Si bond is breaking and a new bond between Si and C is forming (Figure 5d). The transition vector is dominated by the SiC distance (0.82 coefficient). The transition structure **5d** is located at ca. 5 kcal mol^{-1} above the complex **5c**. Consistent with the relative energies of the homolytic and heterolytic dissociation limits, the intermediate **5c** is described as an association of formaldehyde and silyllithium (and not of the formaldehyde radical anion with the lithium cation and the silyl radical). Even if the reacting system were inclined to follow in small

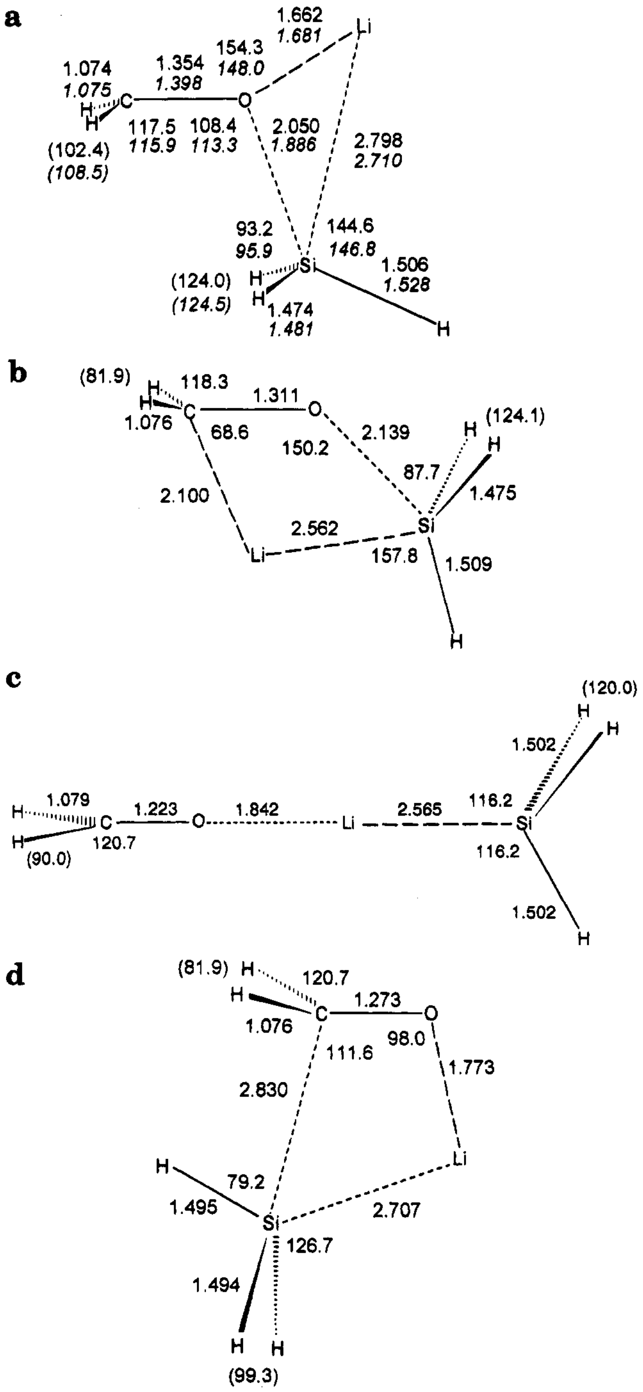

Figure 5. Dissociation–reassociation pathway: (a) first transition structure, connecting (siloxymethyl)lithium **1a** with the electrostatic complex **5c** (MCSCF/3-21G(*) results in italic; see text); (b) second transition structure connecting the secondary minimum of (siloxymethyl)lithium **1c** with **5c**; (c) the electrostatic complex; (d) transition structure leading to lithium silylmethoxide **4b**. Dihedral angles (reported in parentheses) are defined for the methylenic hydrogens as in Figure 3. In the silyl group the dihedral angles are HSiOH, for (a) and (b), while for (c) they are HSiLiH; for (d) they are defined as HSiCH.

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[14] In this computation the 3-21G(*) basis set was used. The active space chosen consists of six orbitals, which were initially defined for two separated fragments, formaldehyde and silyllithium (the geometrical parameters for each fragment were taken from the Hartree–Fock-optimized transition structure geometry). Two active orbitals belong to the formaldehyde fragment, the quasi-π and quasi-π^* couple; four belong to the silyllithium fragment, the σ and σ^* couple pertaining to the Si–Li bond and a σ, σ^* couple of orbitals localized on the silyl group. In this space a complete CI was performed (175 configurations).

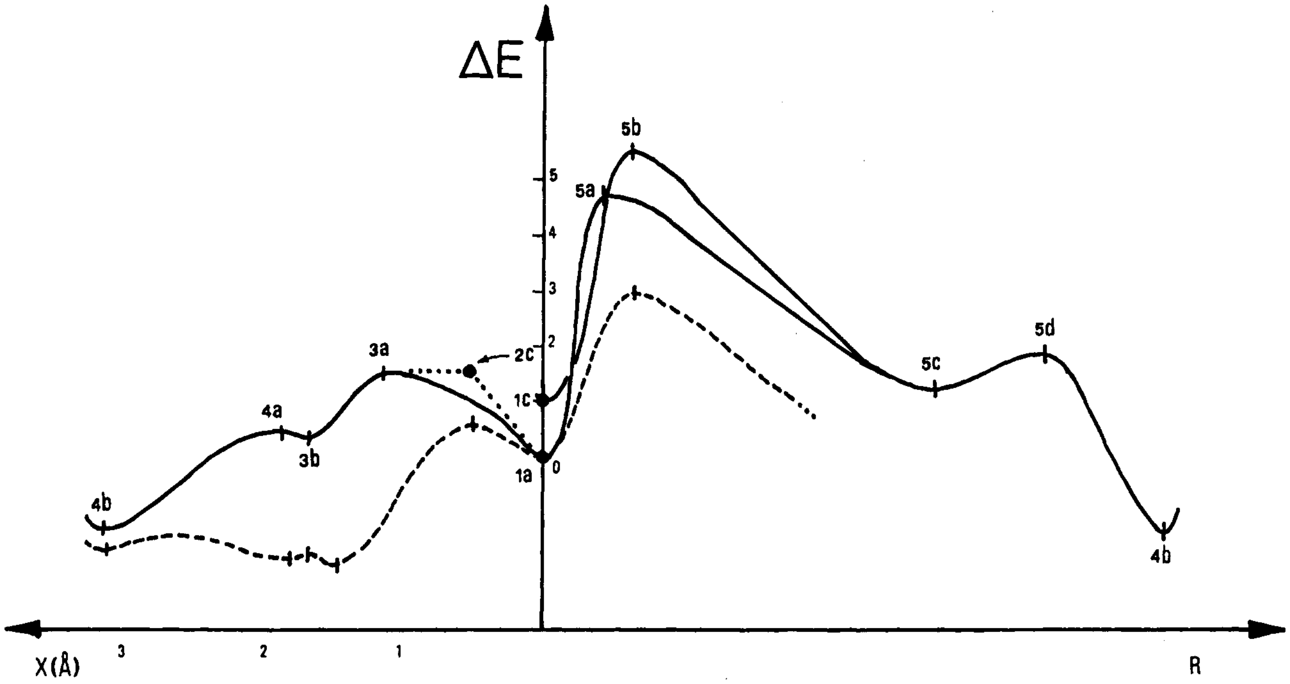

Figure 6. MP3/6-31+G(d)/RHF/3-21+G(*) energy profiles. Left: the nondissociative migration pathway (as a function of the silicon shift projected onto the CO bond axis, X coordinate; origin in correspondence of the initial carbanion). This pathway is reported for the lithiated system (solid line) and for the free anion (dashed line). Right: the dissociation–reassociation pathway (along a symbolic reaction coordinate, R) for the lithiated system (solid line); for sake of comparison, the dissociation curve of the free carbanion is also reported (dashed line).

Table 2. Comparison of the Nondissociative and Dissociative Processes[a] at Various Theoretical Levels[b]

	3a	5a
MP2	13.8	43.3
MP3	14.9	46.9
MP4(DQ)	15.3	48.6
MP4(SDQ)	15.2	47.8
MP4(SDTQ)	14.4	41.7
CCSD	15.2	48.0
CCSD(T)	14.5	41.3

[a] The energy barrier relevant to the transition structure for the nondissociative process (**3a**) and the energy difference between the dissociative transition structure **5a** and the lithiated carbanion **1a** are reported (kcal mol^{-1}). [b] MP method: see ref 8a. Coupled cluster (CC) method: see ref 8b. The 6-31+G(d) basis set has been used throughout.

part a dissociation–reassociation pathway, this result would indicate, in accord with a recent experimental study by Linderman and Ghannam,[15] that radical intermediates are not involved in the Wright–West migration reaction (incidentally, it can be mentioned that the authors indicate that this rearrangement is an intramolecular process). However, up to this point, the barriers for dissociation from the lithiated carbanion have been estimated to be much higher than the energy barriers the system has to overcome in the nondissociative process. In order to get a further check on the relative magnitude of these energy differences, coupled cluster calculations[8b] at the CCSD(T) level[10] were carried out on the more stable structure of the lithiated carbanion (**1a**) and on the two transition structures **2a** and **4a**. These computations also allow examination of the energy differences obtained at various levels of the MP theory,[8a] from MP2 to MP4(SDTQ).[10] These data are collected in Table 2, and show a rather satisfactory consistency of the difference in barrier heights between the two pathways compared. All the results obtained seem to rule out the dissociation–reassociation pathway altogether. Therefore, the mentioned experimental result[15] is rather to be related to the mechanism of rearrangement suggested by the present calculations (a direct shift of the silyl group). Comparing the results obtained for the free anion in paper 1, it can be noted that dissociation has in fact become more difficult: lithium, although involved in this process, does not stabilize the transition structure **5a** relative to the "reactant" **1a**.

The results obtained in this study and in paper 1 are summarized in the energy profiles reported in Figure 6.

Conclusions

The model reactions described in paper 1 and in the present study correspond to two extreme situations of nointeraction and tight interaction of the anionic system with the counterion. In both cases the direct silyl [1,2] migration is found to take place in two kinetic steps, passing through a cyclic intermediate, in which silicon is pentacoordinate. Lithium stabilizes the cyclic intermediate less than the carbanionic reactant and the oxianionic product, raising as a consequence the first energy barrier, but it does not affect significantly the overall reaction exothermicity. The presence of the counterion opens to the initial (H_2COSiH_3)Li open-chain lithiated carbanion the possibility of a dissociative process for the O–Si bond, taking place without complete separation of the H_2CO and SiH_3 fragments, which can be held together by the cation. However, the intervention of Li$^+$ cannot be seen as true *assistance*, because its interaction with the carbon and oxygen atoms in the "reactant" is more stabilizing than that with the oxygen and silicon atoms which operates in the more stable transition structure for dissociation. As a consequence, the energy barrier for dissociation is found to be higher

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(15) Linderman, R. J.; Ghannam, A. *J. Am. Chem. Soc.* **1990**, *112*, 2392–2398.

than that for silyl [1,2] migration also in the presence of Li^+. The two sets of results presented in this study and in the preceding one suggest that, even in conditions of different degrees of anion–cation interaction, the mechanism of the Wright–West rearrangement is to be described as a two-step nondissociative shift of the silyl group.

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