

Articles

Ab Initio Theoretical Investigation on the Wright-West and Wittig Anionic Migration Reactions

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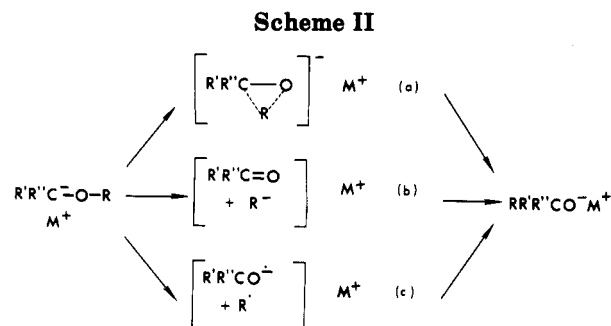
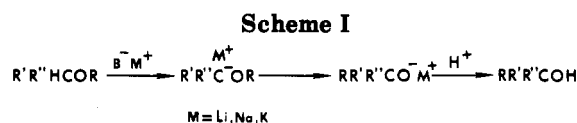
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The carbanion to oxyanion rearrangements in the $(\text{H}_2\text{COSiH}_3)^-$ and $(\text{H}_2\text{COCH}_3)^-$ model systems have been studied. In the case of silicon the direct [1,2] migration takes place in two steps with low energy barriers, passing through a cyclic intermediate species in which silicon is pentacoordinate. In contrast, the model carbon [1,2] migration goes through a single transition structure and, although very exothermic, presents a significantly higher energy barrier. An estimate of the energy barriers for methyl and silyl dissociation shows that the former is preferred over a methyl [1,2] shift, while the latter is much more difficult than silyl [1,2] migration. The remarkable differences between the two reaction energy profiles lie in the stability of the silicon cyclic intermediate. The significant strain introduced as a result of pentacoordination within a cyclic structure is overcome by the ability of the silyl group as a whole to delocalize to some extent the negative charge of the system through bonding interactions with the H_2CO group.

Introduction

The well-known Wittig rearrangement¹ is the transformation of an ether into its isomeric alcohol, through a [1,2] anionic shift of an alkyl, aryl or allylic group (Scheme I). This reaction takes place in the presence of a strong base (such as sodium amide or excess alkyllithium reagent) or alkali metals: the ether, then metalated in the α position, gives rise to an alkali metal alkoxide. The following hypotheses were originally considered for the mechanism of this rearrangement:² (i) a concerted process taking place through a pentacoordinate transition state (Scheme IIa); (ii) a two-step dissociative process involving the formation of a carbanion (heterolytic cleavage of the C-O bond, Scheme IIb) followed by recombination of the two fragments; and (iii) a similar process involving the formation of a pair of radicals and their subsequent recombination (Scheme IIc).

Of these three hypotheses, only the last has recently been believed to be in accord with the experimental evidence.³ Stereochemical findings were considered to oppose the one-step mechanism.^{3a} The radical path was then preferred over the carbanion path on the basis of (a) the ease of migration of different groups,^{3b} reflecting the



relative stabilities of the radicals rather than those of the organolithium compounds, (b) the migration tendency of alkyl groups, reflecting the rate of formation of alkyl radicals,^{3c} and (c) the detection of a chemically induced proton spin polarization in the NMR spectrum of phenyl *tert*-butyl methoxide^{3d} (the interpretation of this last result has been criticized by Dewar).⁴

A similar anionic rearrangement, in which trialkylsilyl is the migrating group, was observed and studied by Wright and West (Scheme III).^{5a} The reaction, occurring when (benzyloxy)organosilanes are treated with excess base (metalation with *t*-BuLi or LDA),⁶ was found to take place

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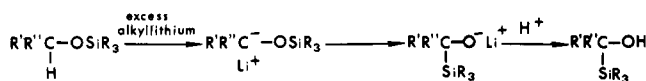
(3) (a) Schollkopf, U. *Angew. Chem., Int. Ed. Engl.* 1970, 9, 763-773. Compare with the discussion in: Garst, J. F.; Smith, C. D. *J. Am. Chem. Soc.* 1976, 98, 1526-1537. (b) Fort, R. C., Jr.; Schleyer, P. v. R. *Adv. Alicycl. Chem.* 1966, 1, 337. Lansbury, P. T.; Sidler, J. D. *Tetrahedron Lett.* 1965, 691-695. (c) Schafer, H.; Schollkopf, U.; Walter, D. *Tetrahedron Lett.* 1968, 2809-2814. (d) for a brief discussion on the usefulness and limits of the CIDNP experiment, see for instance: Carpenter, B. K. *Determination of Organic Reaction Mechanisms*; Wiley: New York, 1984.

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Scheme III

Wright - West



more rapidly than the Wittig migration.^{5a} It also takes place on other substrates.^{5b} A recent mechanistic study^{5c} has indicated that it is an intramolecular process, not involving radical intermediates.

Both the Wittig and Wright-West rearrangements belong to a vast class of [1,2] shifts to an atom with a lone pair.^{3a} These systems are isoelectronic and could in principle all proceed by the same mechanism; however, if two or more mechanisms can compete to some extent, then the balance may lie in favor of one or the other path for different systems.

The primary purpose of the present investigation was to define the gas-phase energy profile for the Wright-West migration, in order to establish if a pentacoordinate silicon intermediate or transition structure is involved (compare Scheme IIa). Several pentacoordinate silicon anions are known.⁷ Trigonal bipyramidal structures are thought to be involved in nucleophilic substitution reactions at silicon^{8a} and can be detected in the gas phase.^{8b} Although the Wright-West rearrangement can be viewed as an S_N reaction, the possibility of a stable pentacoordinate intermediate does not appear to be obvious, as it would most likely be a strained cyclic structure, with a very small CSiO angle at the silicon bridgehead.^{5a} The direct [1,2] silicon shift will be compared with a similar carbon shift, such as could in principle be modeled for the Wittig migration, and the dissociation processes in the two "reactant" carbanions will be studied. This study is articulated in two parts. This paper, dealing with the rearrangements of the α-carbanions derived from the ether or the alkoxy silane, presents an extreme situation in which the interaction with the counterion is absent. In a subsequent paper the same rearrangements will be studied in the presence of a lithium counterion,⁹ which can be bound either to carbon or to oxygen (or both) during the

migration process.¹⁰ The second part will therefore provide another extreme picture of the evolution of these systems, allowing an investigation into the possible role of the counterion in affecting the rearrangement mechanism.

Methods

The study of the reaction hypersurfaces for the two anionic [1,2] shifts has been performed by determining and characterizing the structures corresponding to the relevant critical points. This has been accomplished by way of complete gradient optimizations¹¹ of the geometrical structures at the Hartree-Fock level of theory,¹² and subsequent computation and diagonalization of the analytical Hessian (calculation of the vibrational frequencies) in correspondence to each critical point. Stable structures correspond to a Hessian index equal to 0 (minima on the surface, no imaginary frequencies), while transition structures correspond to a Hessian index equal to 1 (first-order saddle points on the surface, one imaginary frequency). The split-valence shell 3-21+G(*) basis set^{13a} has been used throughout. This basis set contains diffuse sp functions on all non-hydrogen atoms and d polarization functions on silicon; in the absence of second-row atoms, as is the case for the Wittig migration, it is therefore just the 3-21+G basis set.^{13a} The relative energies for the species involved in these reactions were computed introducing correlation effects through perturbative MP3 energy computations,¹⁴ using the split valence shell 6-31+G(d) basis set^{13b} (containing both diffuse sp functions and d polarization functions on all non-hydrogen atoms) in conjunction with the 3-21+G(*) geometries. Configuration interaction calculations were also carried out in some cases, with the purpose of obtaining qualitative interpretations; some computational details will be provided when discussing the results thus obtained (following section). The computations were performed using the Gaussian series of programs¹⁵ on the IBM 3090 computer at CSI-Piemonte (Torino, Italy) and on a VAX Station 3200+3150 cluster at the Istituto di Chimica Organica.

Results and Discussion

The Model Wright-West Rearrangement. The mechanism for the direct transposition of the silyl group is described by the present computations as a two-step

(6) (a) When only a catalytic amount of base is present, the migration takes place in the opposite (anti-Wittig) direction (Scheme III) giving alkoxy silanes from α-silylcarbinols (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.; Pascoe, J. D. *J. Am. Chem. Soc.* 1971, 93, 6224-6227. Brook, A. G. *Acc. Chem. Res.* 1974, 7, 77-84. Thus, the rearrangement studied in this paper is also called silyl-Wittig or reverse Brook rearrangement. (b) Wilson, S. R.; Hague, M. S.; Misra, R. N. *J. Org. Chem.* 1982, 47, 747-748. Hudrlik, P. F.; Hudrlik, A. M.; Kulkarni, A. K. *J. Am. Chem. Soc.* 1982, 104, 6809-6811.

(7) See, for instance: Frye, C. L.; Vogel, G. E.; Hall, J. A. *J. Am. Chem. Soc.* 1961, 83, 996-997. Corriu, R. J. P.; Guerin, C.; Henner, B. J. L.; Wang, Q. *Organometallics* 1991, 10, 2297-2303, 3200-3205, 3574-3581 and references cited therein. For a recent study on stable pentacoordinate silicon species, see: Damrauer, R.; Burggraf, L. W.; Davis, L. P.; Gordon, M. S. *J. Am. Chem. Soc.* 1988, 110, 6601-6606.

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(9) If none of the three mechanisms is completely discarded *a priori*, and if they are thought to compete to some extent, then the role of the counterion can have a different importance in stabilizing the intermediate species or the transition states. The influence that the counterion (usually lithium) may have on the mechanism of this migration process depends in principle on a number of factors, for instance, the nature of the solvent, namely its electron-donating capability, or the presence of complexing agents. See, for instance: Hebert, E.; Welvart, Z.; Ghelfenstein, M.; Szwarc, H. *Tetrahedron Lett.* 1983, 24, 1381-1384.

(10) The cation is generally considered to form with the anion a contact or solvent-separated ion pair; the lithium-carbon bond (that can be present in the metalated ethers) is considered an ionic bond, or at least a bond with a high degree of ionicity. See: Reed, A. E.; Weinstein, R. B.; Weinhold, F. *J. Chem. Phys.* 1985, 83, 735-746. Francl, M. M.; Hout, R. F.; Hehre, W. J. *J. Am. Chem. Soc.* 1984, 106, 563-570. Streitwieser, A.; Collins, J. B. *J. Comput. Chem.* 1980, 1, 8. Graham, G. D.; Marynick, D. S.; Lipscomb, W. N. *J. Am. Chem. Soc.* 1980, 102, 4572-4578. Hincliffe, A.; Saunders, E. J. *Mol. Struct.* 1976, 31, 283. Streitwieser, A., Jr.; Williams, J. E.; Alexandratos, S.; McKelvey, J. M. *J. Am. Chem. Soc.* 1976, 98, 4778-4784.

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(12) The Hartree-Fock level of theory is expected to yield sufficiently realistic geometrical structures because bond breaking and bond making take place simultaneously during the concerted migration process, as in S_N2 reactions. A perturbative treatment of electron correlation effects on the total energy should therefore be adequate for defining a qualitatively correct energy profile. When studying dissociative processes (see text), the geometry optimizations were done at the MC-SCF level of theory (see ref 21).

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(14) Møller, C.; Plesset, M. S. *Phys. Rev.* 1934, 46, 618. Binkley, J. S.; Pople, J. A. *Int. J. Quantum Chem.* 1975, 9, 229. Krishnan, R.; Pople, J. A. *Int. J. Quantum Chem. Symp.* 1980, 14, 91.

(15) Gaussian 82: Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Krishnan, R.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. Carnegie-Mellon Chemistry Publ. Unit. Gaussian 88: Frisch, M. J.; Head-Gordon, M.; Schlegel, H. B.; Ragavachari, K.; Binkley, J. S.; Gonzalez, C.; DeFrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R.; Kahn, L. R.; Stewart, J. J. P.; Fluder, E. M.; Topiol, S.; Pople, J. A. Gaussian Inc., Pittsburgh, PA, 1988.

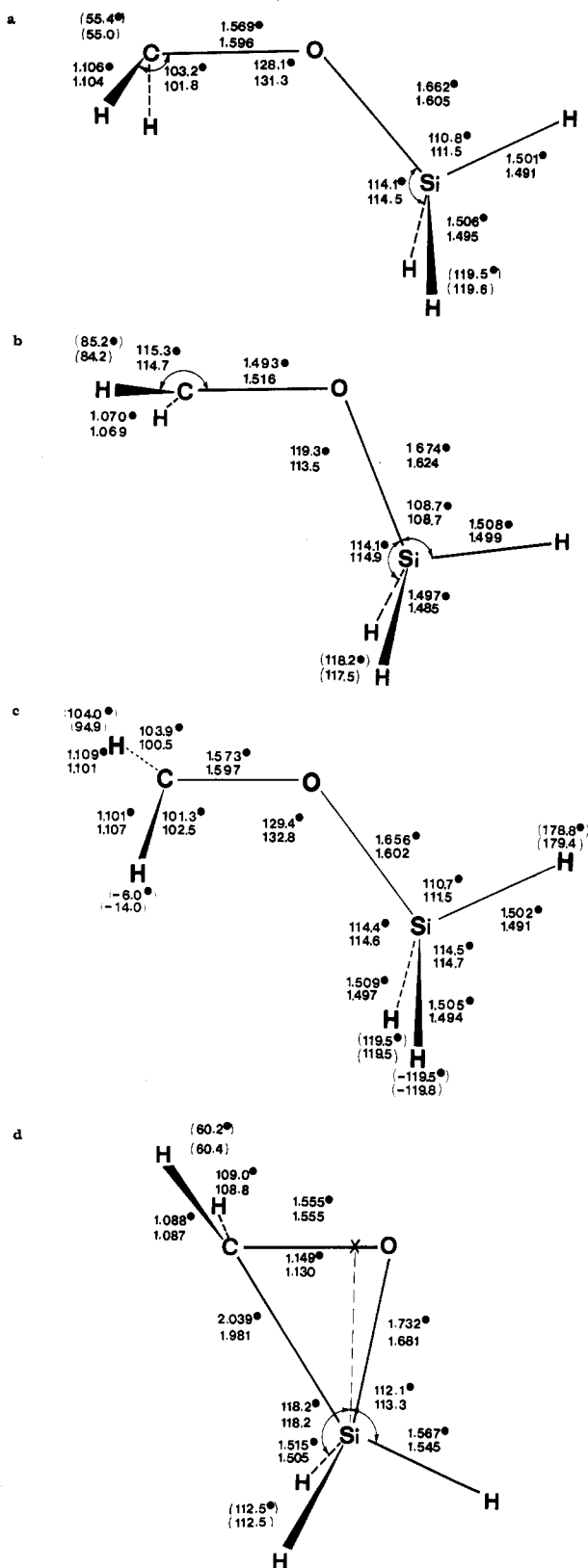


Figure 1. Optimized geometrical parameters corresponding to the critical points on the hypersurface for the Wright-West migration (H_2COSiH_3 model system): (a) the carbanionic minimum; (b) transition structure with CH_2 inversion; (c) transition structure with CH_2 rotation; (d) the cyclic minimum "A". Bond lengths in Å, angles in deg. HCOSi and HSiO (in-plane H) dihedral angles in parentheses. RHF/3-21+G(*) and 3-21+G (dotted) values.

migration passing through a stable cyclic intermediate. The "reactant" siloxymethanide (Figure 1a) is the carbanion originating from silyl methyl ether through depro-

tonation. The structure shown corresponds to a conformation in which the carbon lone pair is antiperiplanar with respect to the O-Si bond. The large SiOC angle can also be found in the silyl ether from which it originates.¹⁶ From this minimum, the cyclic intermediate can be reached through two different transition structures. The first one is shown in Figure 1b: the transition vector is dominated by the inversion motion of the CH_2 hydrogens coupled with the motion of the silyl group parallel to the C-O bond. It can be seen that the silicon atom is still much closer to the oxygen than to the carbon atom. The second transition structure (Figure 1c) corresponds to a rotation of the CH_2 group and might connect 1a with another carbanionic structure in which the carbon lone pair is synperiplanar to the O-Si bond. This second conformational minimum for the carbanion has not been found, however; any attempt to define such a structure leads to ring closure, i.e., formation of a C-Si bond, without any energy barrier. Diagonalization of the analytical Hessian shows a transition vector with pure CH_2 rotation components and no component relevant to a silicon migration motion. The energy barrier corresponding to 1c is lower than that of 1b (Table I). The two transition structures just discussed both lead to a cyclic intermediate, in which silicon is pentacoordinate (Figure 1d). This minimum, where the silyl group is staggered with respect to the O-C bond in the H_2CO group, as it was in the carbanion and in the transition structures, will be labeled "A". A cyclic structure had already been suggested as a possible transition state or intermediate in some studies of silicon migrations.^{5,6} Considering the S_N nature of this rearrangement, the presence of a pentacoordinate silicon intermediate is in accord with the current views on nucleophilic substitution at silicon.⁷ The first part of the migration path is exothermic by almost 19 kcal mol⁻¹, and in accordance with the Hammond postulate, the transition structures are geometrically closer to the initial carbanion than to the cyclic intermediate. The reasons for the relative stability of this intermediate (in which the CSiO angle is ca. 49°) will be discussed in the following paragraphs.

In order to determine whether the presence of d functions on silicon plays a role in stabilizing the cyclic structure¹⁷ (or even determining its existence and the topology of this first portion of the surface) the structures of the four critical points shown in Figure 1 have been reoptimized with the same sp basis set, but without Si d functions. The qualitative description of this part of the reaction path does not change.^{18a} The existence of a cyclic intermediate cannot be attributed to the intervention of silicon d functions; nevertheless, their use appears to stabilize the cyclic structure with respect to the carbanion by ca. 3 kcal mol⁻¹ (RHF energies, Table I).^{18b}

Minimum A is not the only minimum corresponding to a cyclic intermediate, because a rotational transition structure (Figure 2a) relates to a second minimum (referred to as "B") where the silyl group is staggered with respect to the O atom in the C-O bond (Figure 2b). This second

(16) Compare the results discussed in: Shambayati, S.; Blake, J. F.; Wierschke, S. G.; Jorgensen, W. L.; Sreiber, S. L. *J. Am. Chem. Soc.* 1990, 112, 697-703.

(17) For simpler systems the possible role of silicon d functions has been tested: for the pentacoordinated stable species SiH_5^- a central role of d orbitals in determining its stability with respect to loss of a hydride ion has been ruled out (although d functions provide an extra stabilization of 8.5 kcal mol⁻¹): Reed, A. E.; Schleyer, P. v. R. *Chem. Phys. Lett.* 1987, 133, 553-561. An interesting discussion on the reasons for the stability of this species can be found in: Sini, G.; Ohanessian, G.; Hiberty, P. C.; Shaik, S. S. *J. Am. Chem. Soc.* 1990, 112, 1407-1413.

Table I. Total^a and Relative^{b,c} Energies of the Critical Points

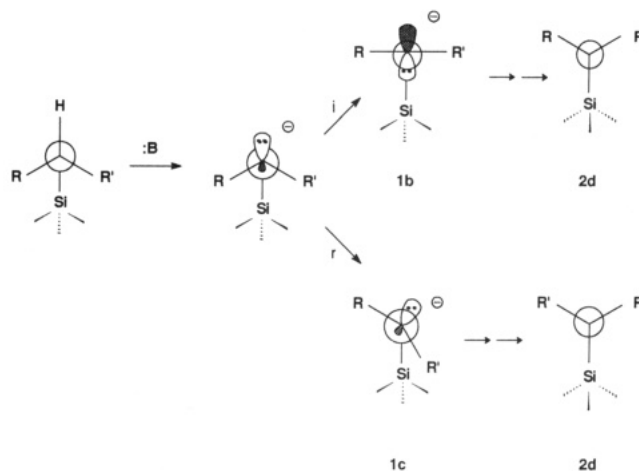
structure		MP3/6-31+G(d) ^d		RHF/3-21+G(*)	
		E	ΔE	E	ΔE
Wright–West Rearrangement					
carbanion	1a	-404.904 480	0.0	-402.458 749	0.0
T.S.	1b	-404.894 432	6.3	-402.443 493	9.6 (8.8)
T.S.	1c	-404.902 978	0.9	-402.458 040	0.4 (0.9)
cyclic anion A	1d	-404.934 402	-18.8	-402.477 042	-11.5 (-8.2)
T.S.	2a	-404.931 433	-16.9	-402.471 976	-8.3
cyclic anion B	2b	-404.932 887	-17.8	-402.472 766	-8.8
T.S.	2c	-404.927 256	-14.3	-402.463 793	-3.2
oxyanion	2d	-404.927 919	-14.7	-402.464 298	-3.5
Wittig Rearrangement					
carbanion	3a	-153.860 314	0.0	-152.561 842	0.0
T.S.	3b	-153.755 007	66.1	-152.441 499	75.5
oxyanion	3c	-153.934 327	-46.4	-152.631 885	-43.9

^a Hartree. ^b kcal mol⁻¹. ^c Wright–West migration; values in parentheses refer to 3-21+G computations. ^d Computed at the RHF/3-21+G(*) optimized geometries.

conformation of the intermediate is slightly less stable than A (Table I). While in A the carbon atom and the in-plane hydrogen appear to occupy approximately apical positions around the pentacoordinate silicon, in B oxygen is displaced by carbon from its equatorial position and occupies a nearly apical position (compare the length of the relevant Si-centered bonds). This exchange results not only in the rotation of the SiH₃ group, but also in the movement of silicon toward carbon (CX distances). In addition, the C–O bond gradually shortens, its value approaching that of the oxyanionic “product”. A third transition structure (Figure 2c) separates B from the product silyl methoxide (Figure 2d). The transition vector in 2c is dominated by the translation of the silicon atom approximately parallel to the C–O bond.

The final oxyanion can thus be obtained by either of two different paths, one involving the transition structure 1b and the other (favored for the simple model studied here) proceeding through the transition structure 1c. If a disubstituted silyl ether HRR'COSiR''₃ were involved in the rearrangement, the stereochemical outcome of the rearrangement would depend on the path followed by the system (Scheme IV). A pathway involving a transition structure similar to 1b would obviously lead to inversion of configuration at the carbon atom bearing the two substituents R and R' (path i). If, on the other hand, the path through a transition structure similar to 1c were preferred, retention of configuration would result (path r). The experimental evidence for the Brook rearrangement^{6a} indicates that alkyl-substituted systems rearrange with retention of configuration,^{6b} while aryl-substituted systems undergo inversion of configuration.^{6a} The same stereochemistry has recently been observed for the Wright–West rearrangement.^{5c} The simple model studied here may be closer to the case of alkyl substitution, and the

Scheme IV



relative height of the two energy barriers (Table I) can provide an interpretation for the observed retention of configuration. An aryl substituent is likely to stabilize planar structures, thus favouring the inversion path.

The overall migration exhibits the character of a frontside S_N attack at silicon, wherein the incoming (hard) nucleophile (C⁻) prefers an apical direction of attack and the leaving group (O⁻) exchanges its original equatorial position for an apical one before the process is completed.¹⁹ As mentioned in the Introduction, trigonal bipyramidal structures with a central pentacoordinate silicon atom are thought to be involved in nucleophilic substitution reactions at silicon.⁸ The two cyclic structures A and B are not expected to be true trigonal bipyramids, mainly because two of the five (different) “ligands” are bound together; in A the CSiH(axial) angle is in fact 148°, and in B the OSiH(axial) angle is 159°. If the departure from the ideal angle of 180° is viewed as a result of the constraint imposed by the cyclic structure, then the strain (or “missing stabilization”) relative to the carbanion can be estimated. This was first attempted by studying a similar frontside nucleophilic reaction in the H₃SiOCH₂⁻ + H₃SiOH system,^{20a} in which no bond exists between the carbon in the nucleophile and the oxygen in the leaving group. The energy drop from the reagents to the pentacoordinate intermediate with equatorial C and axial O (to be compared with cycle B, 2b) is 44 kcal mol⁻¹, at the RHF/3-21+G(*)

(18) (a) The optimized geometrical parameters obtained using both basis sets are reported in Figure 1a–d. The differences between the 3-21+G (dotted values) and 3-21+G(*) geometries are not very large, consisting mainly in longer CO bonds in 1a and 1b and tighter silicon-centered groups when d functions on silicon are present: i.e., shorter SiO, SiH, and (in the cyclic intermediate) SiC bonds. (b) For the role of d functions on isomerization energies, see: Flanagan, M. C.; Komornicki, A.; Mc Iver, J. W., Jr. In *Modern Theoretical Chemistry*; Schaefer, H. F., Ed., Plenum: New York and London, 1977; Vol. 4, Chapter 8. (c) The energy differences for the two migration processes, recomputed at the MP3/6-31+G(d) level, suggest that the energy profile is already correctly represented, from a qualitative point of view, at the RHF level of theory. Correlation lowers the energy not only of the transition structures but also of the cyclic minima; it appears therefore to preferentially stabilize the more “crowded” arrangement with respect to the open structures; compare for instance: Tonachini, G.; Bernardi, F.; Schlegel, H. B.; Stirling, C. J. M. *J. Chem. Soc., Perkin Trans. 2* 1988, 705–709.

(19) The results of Deiters and Holmes on nucleophilic substitution at silicon can be compared: Deiters, J. A.; Holmes, R. R. *J. Am. Chem. Soc.* 1987, 109, 1686–1692 and 1692–1696. Deiters, J. A.; Holmes, R. R.; Holmes, M. H. *Ibid.* 1988, 110, 7672–7681.

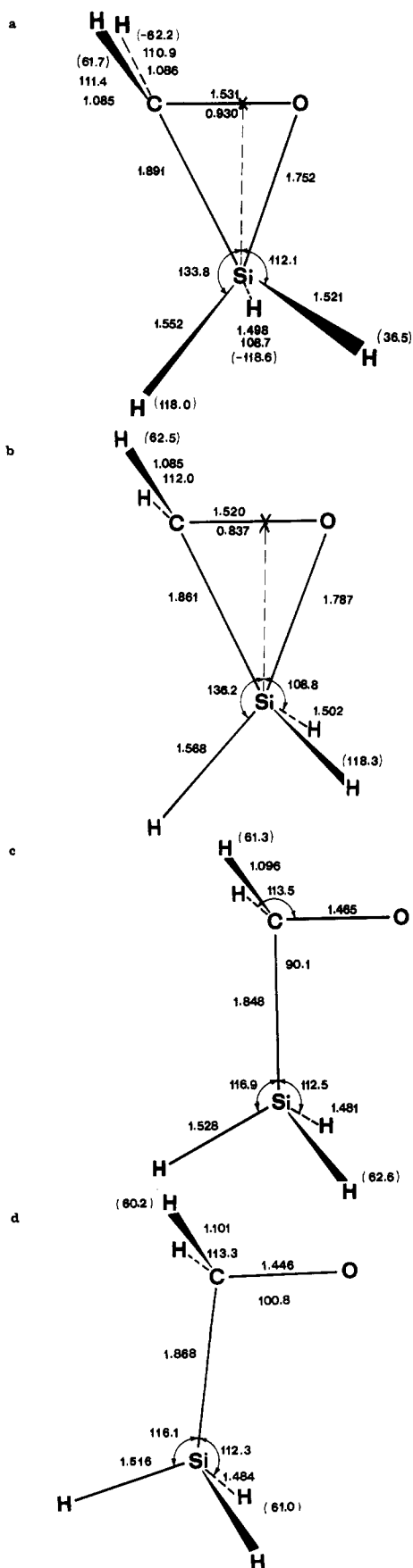


Figure 2. Optimized geometrical parameters corresponding to the critical points on the hypersurface for the Wright-West migration (H_2COSiH_3 model system): (a) rotational transition structure; (b) the cyclic minimum "B"; (c) transition structure for ring opening; (d) the oxyanionic minimum. Bond lengths in Å, angles in deg. HCOSi , HSiCO , and HSiXO dihedral angles in parentheses. RHF/3-21+G(*) values.

level. Comparing this figure with that reported in Table I for cycle B, the "missing stabilization" due to the constraint of having the nucleophile and leaving group bound together can be roughly estimated to be 35 kcal mol⁻¹. As a more reliable alternative, the strain energy can be estimated by computing the energy difference for the homodesmotic reaction^{20b} $(\text{CH}_3\text{SiH}_3\text{OH})^- + \text{SiH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{OSiH}_3 \rightarrow (c\text{-CH}_2\text{SiH}_3\text{O})^- + \text{CH}_3\text{SiH}_3 + \text{SiH}_3\text{OH} + \text{CH}_3\text{OH}$, in which the open-chain anion can approximately be in either the axial-C/equatorial-O arrangement or in the equatorial-C/axial-O arrangement. Using this method a lower (but still significant) estimate of the "missing stabilization" is obtained. In the first case the cycle on the right hand of the equation is cycle A (1d), and the strain energy is computed to be approximately 18.2 kcal mol⁻¹; in the second case it is cycle B (2b), and the estimate of the strain energy is 21.2 kcal mol⁻¹. Thus, these computations provide the picture of a cyclic structure which exists as an intermediate, notwithstanding the strain to which it is subjected.

The Model Wittig Rearrangement. The Wittig migration has been studied in a parallel fashion, with the purpose of comparing a model direct carbon [1,2] shift with the silicon shift just discussed. The nondissociative migration of the methyl group shows remarkable differences both in the qualitative description of the relevant energy hypersurface (nature and geometrical features of the critical points found) and in the energetics (Table I).^{18c} The following structures have been determined: the carbanion originating from dimethyl ether, methoxymethanide (Figure 3a); a transition structure for the [1,2] migration process (Figure 3b); and the oxyanionic product, ethoxide (Figure 3c).

The transition vector qualifies the structure shown in Figure 3b as the transition structure for a concerted migration process. The energy barrier at the RHF level is high, ca. 76 kcal mol⁻¹; of these, 63 kcal mol⁻¹ are still present in the nonstrained model (built in the same way as for silicon),^{20a} setting the approximate estimate of the strain contribution to the barrier at ca. 12 kcal mol⁻¹, much less than in the silicon case. Again, using a homodesmotic reaction^{20b} to estimate the strain energy, this figure is reduced to 5.2 kcal mol⁻¹. While the "reactant" methoxymethanide and the "product" ethoxide (Figure 3a,c) have counterparts in the "reactant" and "product" of the Wright-West migration, the structural parameters of 3b are of course very different from those of the transition structures found in the Wright-West migration. Structure 3b might be compared to some extent with the rotational transition structure 2a for the silicon migration, because

(20) (a) Unpublished results. The migrations discussed in the present paper present a close similarity to a nucleophilic substitution reaction, where carbon displaces oxygen through a "frontside" attack on the central atom of a methyl or silyl group: apart from ring strain, the electronic factors governing these reactions must be basically the same. Indeed, while the model gas-phase $\text{S}_{\text{N}}2$ displacement $\text{H}_3\text{COCH}_2^- + \text{CH}_3\text{OH} \rightarrow \text{H}_3\text{COCH}_2\text{CH}_3 + \text{OH}^-$ presents a first-order saddle point in correspondence to a structure with pentacoordinate central carbon atom, the analogous nucleophilic attack on silicon, $\text{H}_3\text{SiOCH}_2^- + \text{SiH}_3\text{OH} \rightarrow \text{H}_3\text{SiOCH}_2\text{SiH}_3 + \text{OH}^-$, goes through an intermediate with pentacoordinate silicon (only the structure where C is equatorial and O is axial has been optimized). (b) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* 1978, 32, 317-323. George, P.; Trachtman, M.; Brett, A. M.; Bock, C. W. *J. Chem. Soc., Perkin Trans. 2* 1977, 1036-1047. For recent examples of computation of ring strain energies using the method of homodesmotic reactions, see: Disch, R. L.; Schulman, J. M.; Sabio, M. L. *J. Am. Chem. Soc.* 1985, 107, 1904-1906. Boatz, J. A.; Gordon, M. S.; Hildebrandt, R. L. *J. Am. Chem. Soc.* 1988, 110, 352-358. Boatz, J. A.; Gordon, M. S. *J. Phys. Chem.* 1989, 93, 3025-3029. Horner, D. A.; Grev, R. S.; Schaefer, H. F., III. *J. Am. Chem. Soc.* 1992, 114, 2093-2098.

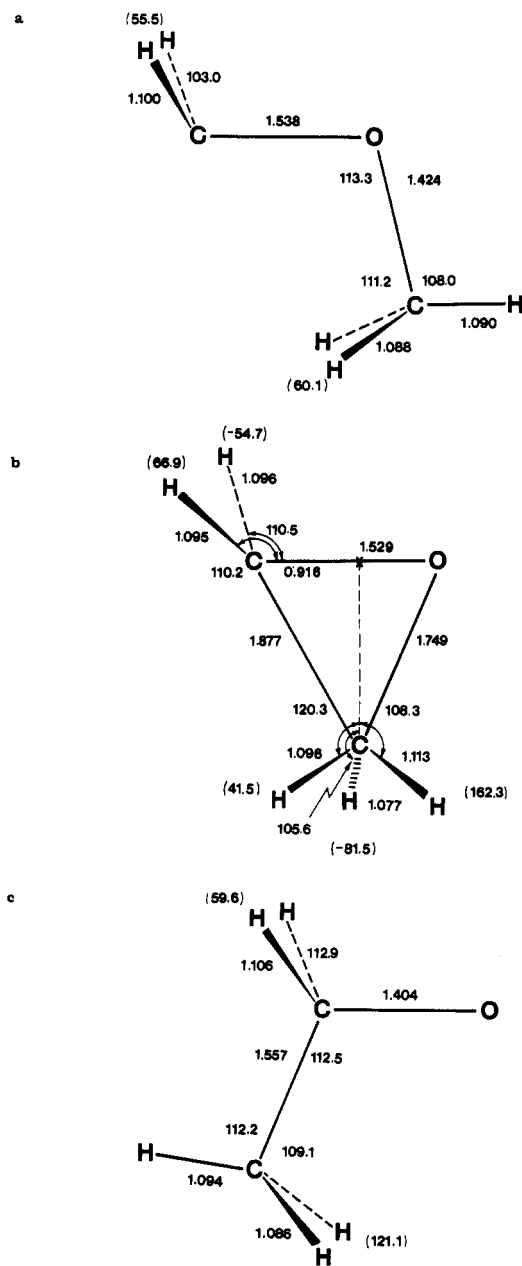


Figure 3. Optimized geometrical parameters corresponding to the critical points of the hypersurface for the Wittig migration (H_2COCH_3 model system): (a) the carbanionic minimum; (b) the transition structure for the [1,2] migration; (c) the oxyanionic minimum. Bond lengths in Å, angles in deg. HCO , HCXC , HCC (in-plane H) dihedral angles in parentheses. RHF/3-21+G values.

the "migration parameter" CX locates them approximately "halfway" between the relevant initial carbanions and final oxyanions, with a similar arrangement of the YH_3 migrating group. Some geometrical features show interesting differences. In **3b** the O-C (methyl carbon) bond is stretched by ca. 23% with respect to the value in the carbanion and the C-C bond by ca. 21% with respect to the value in the oxyanion; in **2a** the O-Si and C-Si values are stretched by only 9% and 1%, respectively. The carbon cyclic transition structure is therefore much looser, with respect to the open forms, than the silicon cyclic transition structure. On one hand the silicon carbanion already has longer Si-centered bonds with respect to its carbon counterpart: a less severe stretching is thus required to accommodate five atoms around silicon. On the other

hand, these different increments suggest a much smaller degree of bonding in the pentacoordinate carbon transition structure.

The energies relevant to the concerted methyl shift (Table I) show that the process, although very exothermic, has a large activation energy, consistent with the classification of this anionic [1,2] rearrangement as symmetry forbidden. The present computations indicate, therefore, as expected and in agreement with the experimental data, that a concerted migration is not likely to occur. Comparing the energy profiles for the two model migrations (Figures 4 and 5, left side), it is apparent that the Wright-West migration does not show the large exothermicity of the Wittig rearrangement, but the computed energy barriers are significantly lower than those found for the concerted methyl migration.^{18c}

Dissociative Processes. Both the Wright-West and the Wittig migrations have been studied in terms of the possible competition of the direct [1,2] shifts with dissociative processes (Figures 4 and 5, right). In the case of silicon (Wright-West migration) the heterolytic dissociation limit (formaldehyde + silyl anion) is energetically close to the carbanion (+1.0 kcal mol⁻¹), while the homolytic (formaldehyde radical anion + silyl radical) is much higher (49.5 kcal mol⁻¹). The estimated²¹ energy barrier for the dissociation process connecting the carbanion to the lower-energy dissociation limit is found to be ca. 30 kcal mol⁻¹. The nature of this barrier is discussed below. Figure 4 shows that in this case migration is much easier, and dissociation is not a competitive process. Therefore, the dissociation/reassociation pathway has not been investigated further in the case of silicon.

In the case of carbon the heterolytic dissociation limit (formaldehyde + methyl anion) is 10.3 kcal mol⁻¹ above the carbanionic minimum, and the homolytic (formaldehyde radical anion + methyl radical) is 14.2 kcal mol⁻¹ higher than the heterolytic. The two dissociation limits are thus closer than in the silicon case. A barrier of ca. 24 kcal mol⁻¹ is estimated²¹ to separate the carbanion minimum from the lower-energy dissociation limit (Figure 5). If this were the only energy barrier, or the higher one, to be overcome in a dissociation/reassociation process, this pathway would of course be preferred over the high energy [1,2] shift concerted migration. An energy minimum, corresponding to an $\text{H}_3\text{C}^-\cdots\text{H}_2\text{CO}$ ion-dipole (ID) complex, is expected to be present on the energy hypersurface. Indeed, ID complexes of this kind are commonly encountered when studying gas-phase models for ionic reactions similar to the reassociation process that can take place in this case;²² on the basis of the results obtained on similar systems, the barrier separating the ID complex from the reassociation product is not expected to be high.²³ How-

(21) The approximate energy profiles for the silyl or methyl dissociation processes from the corresponding carbanions were obtained by single-point MP3 energy computations at various O-X distances (X = Si, C). The geometries of the H_2CO and XH_3 fragments were optimized at each interfragment distance by MC-SCF computations,²⁰ using four active orbitals (see the Qualitative CI Analysis section in the text for details on the definition of the active space).

(22) See, for instance: (a) Bernardi, F.; Olivucci, M.; Poggi, G.; Robb, M. A.; Tonachini, G. *Chem. Phys. Lett.* 1988, 144, 141-144. (b) Tonachini, G.; Bernardi, F.; Schlegel, H. B.; Stirling, C. J. M. *J. Chem. Soc., Perkin Trans. 2* 1988, 705-709.

(23) In the case of the $\text{OH}^- + \text{H}_2\text{CO}$ reaction (ref 22a) the energy barrier separating the ID complex from the intermediate HOCH_2O^- was estimated to be 1.5 kcal mol⁻¹ (RHF/3-21+G) or 2.9-3.8 kcal mol⁻¹ (MCSCF/3-21+G, computed with two different active spaces; see ref 22a for details). In the case of the $\text{H}_3\text{C}^- + \text{H}_2\text{CCH}_2$ system (ref 22b) the analogous barrier was calculated to be 11.7 kcal mol⁻¹ (RHF/6-31+G(d))/3-21G) or 4.4 kcal mol⁻¹ (MP2 computations; see ref 22b for details).

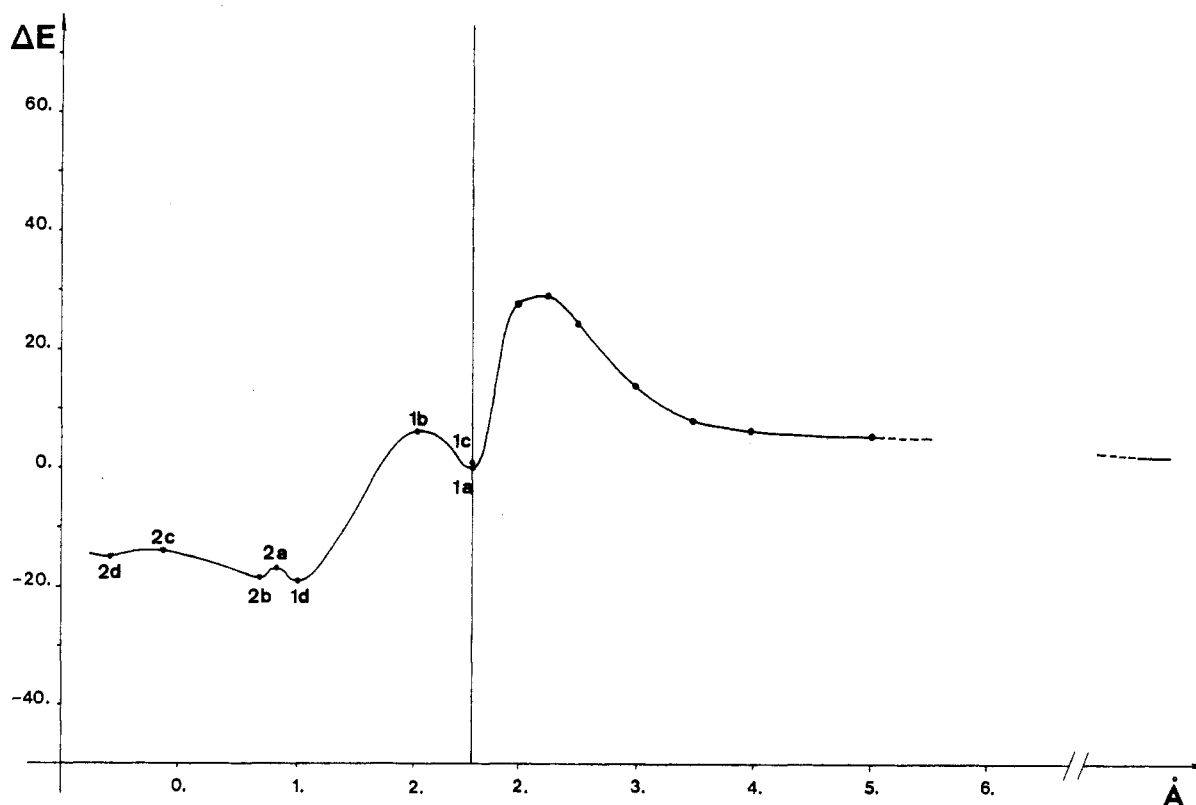
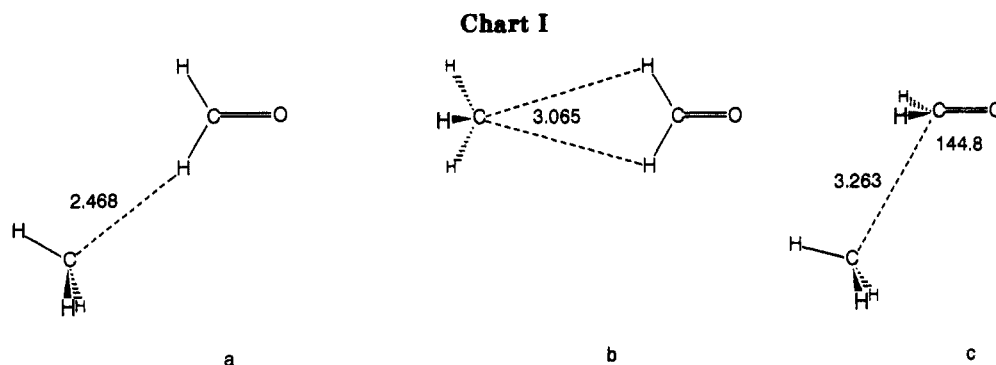


Figure 4. Left: the energy profile for the Wright-West migration reaction (H_2COSiH_3 model system) as a function of the silicon shift projected onto the C-O bond axis (origin in C, abscissa values in Å). MP3/6-31+G(d) energy values in correspondence to the 3-21+G(*) critical point geometries. Right: MP3/6-31+G(d) approximate (see text) silyl dissociation energy profile in the carbanion. Abscissa values, in Å, refer to the O-Si distances.



ever, in this case dissociation may be the preferred pathway, and it could be worthwhile to complete its description by assessing the stability of the ID complex with respect to the reactant, and estimating the energy barrier that separates it from the oxyanion 3c. Two equivalent energy minima are found which correspond to stable structures in which the negative methylic carbon is coplanar with the formaldehyde molecule and interacts with one of the two hydrogens (one of them is shown in Chart Ia).

The deviation from C-H-C collinearity is reflected in the CCO angle (145.4° , to be compared with the formaldehyde HCO angle in the complex, 125.6°). The ID complex is rather stable: $3.3 \text{ kcal mol}^{-1}$ below the carbanion 3a at the MP3 level (-2.1 at the RHF level). These two minima are separated by a tiny energy barrier ($0.3 \text{ kcal mol}^{-1}$, computed at the RHF level only). In the relevant transition structure (Chart Ib) the methyl carbon is collinear with the C-O bond. The methyl group is almost free to rotate in both the complexes and the transition structure. All "intrafragment" geometrical parameters are

very close to those found for the two separate molecules. It can be seen that the region of the energy hypersurface wherein stabilizing ion-dipole interactions between formaldehyde and a coplanar negative methyl carbon are effective is rather flat and extended. A transition structure for the nucleophilic attack of the CH_3^- anion on the formaldehyde carbon (Chart Ic) is found to occur at a large C-C distance (consistent with a significant exothermicity of this step: $-43.1 \text{ kcal mol}^{-1}$). The energy barrier for reassociation is estimated to be very low ($0.5 \text{ kcal mol}^{-1}$) at both the RHF and MP3 levels. Therefore, the reassociation step is not crucial for discussing the preferred mechanism of rearrangement. The methyl dissociation process reported in Figure 5 takes place in a plane perpendicular to the C-HCO plane in the ID complex, and the methyl group is described as moving away from the ID complex region; for this reason, there is no trace of this minimum in that approximate energy plot. Nevertheless, the dissociating methyl anion is likely to fall in the lower energy region of the surface before being able to recombine with the H_2CO moiety. In conclusion,

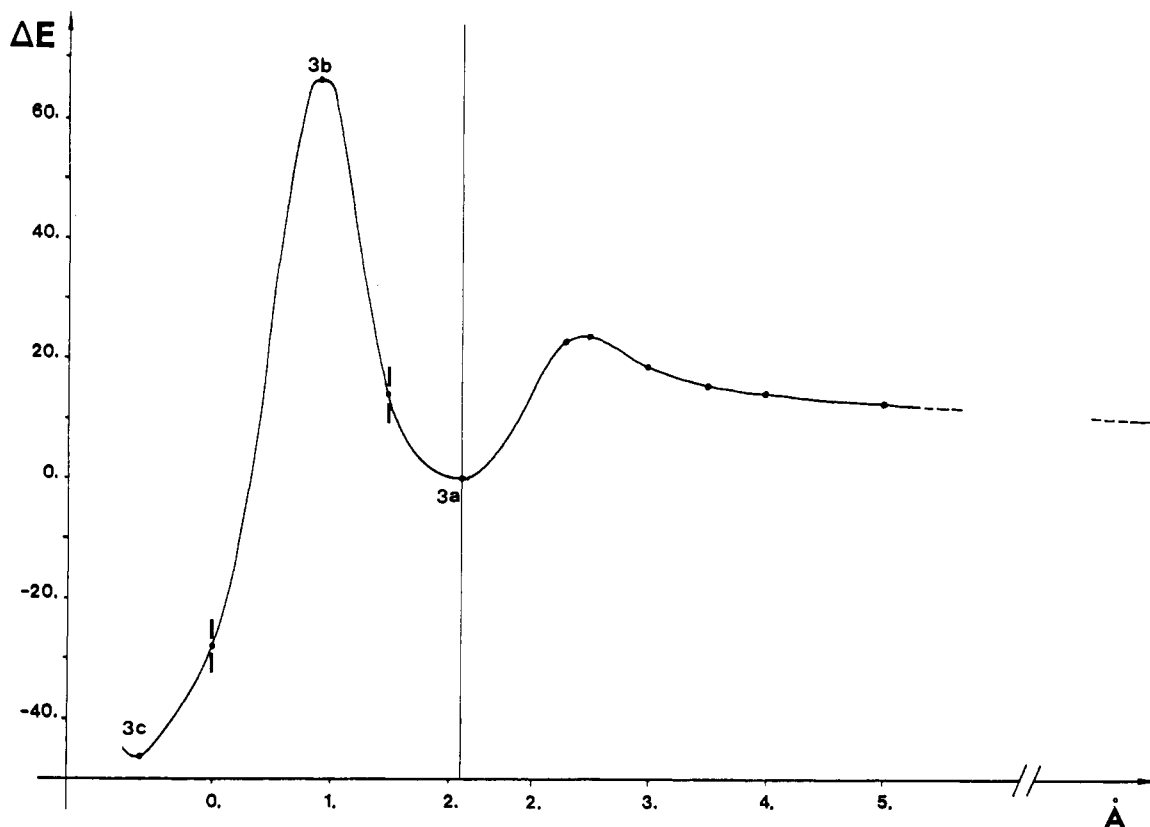


Figure 5. Left: the energy profile for the Wittig migration reaction (H_2COCH_3 model system) as a function of the methyl carbon shift projected onto the C–O bond axis (origin in C, abscissa values in Å). MP3/6-31+G(d) energy values in correspondence to the 3-21+G critical point geometries. --- marks additional noncritical points.²⁸ Right: MP3/6-31+G(d) approximate (see text) methyl dissociation energy profile in the carbanion. Abscissa values, in Å, refer to the O–C(methyl) distances.

Table II. NAO Charges^a in the Open-Chain Carbanions and Cyclic Structures^b

		H	H	C	O	X	H	H	H
X = Si	1a	0.098	0.098	-0.619	-1.125	1.496	-0.310	-0.318	-0.318
	1d	0.153	0.153	-0.623	-1.035	1.360	-0.378	-0.316	-0.316
	2a	0.148	0.149	-0.631	-1.020	1.357	-0.346	-0.347	-0.309
X = C	2b	0.171	0.171	-0.607	-1.035	1.282	-0.389	-0.296	-0.296
	3a	0.109	0.109	-0.705	-0.774	-0.199	0.146	0.158	0.158
	3b	0.125	0.128	-0.482	-0.915	-0.337	0.119	0.201	0.161

^a See ref 25. ^b Computed with the 6-31+G(d) basis set at the RHF/3-21+G(*) optimized geometries.

dissociation followed by reassociation appears to be much easier than the model concerted Wittig migration; however, the computational results for the gas-phase reaction, indicating heterolytic dissociation, appear to be only partially in accord^{24a} with current views on the mechanism of this rearrangement, which is thought to take place in a nonconcerted way via formation/recombination of two radicals, remaining in the same solvent cage during the migration.³

Electron Distribution in the Cyclic Structures.

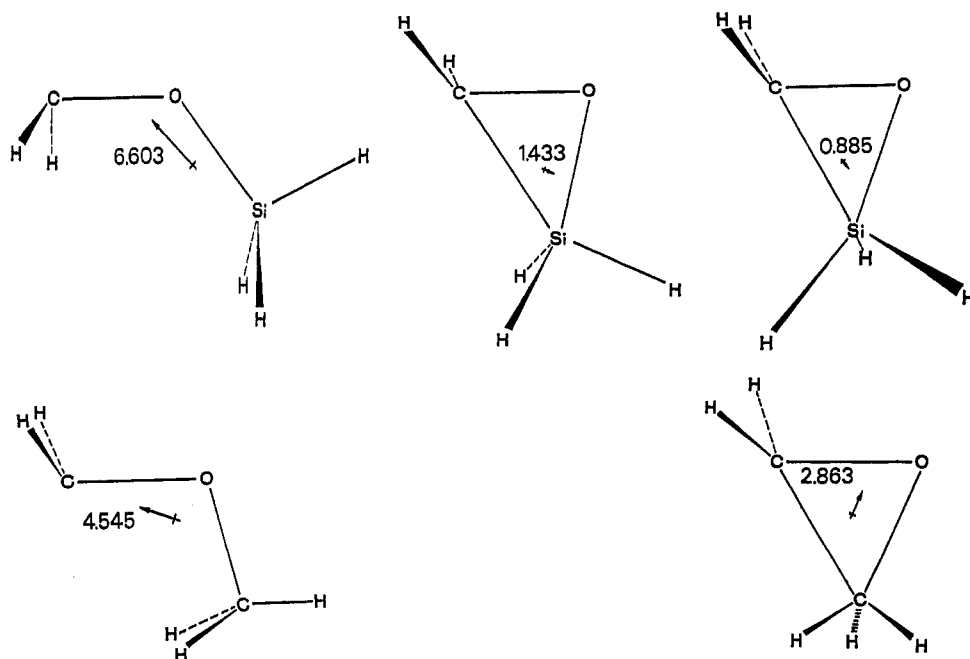
The energy differences between the two dissociation limits show that the silyl group is much more inclined than methyl to accept an extra electron (with the "donor" H_2CO group as a reference). This feature is not expected to be retained at bonding distances, due to the low electronegativity of silicon; indeed, the RHF/6-31+G(d) atomic charges obtained by the natural atomic orbital (NAO) population

analysis method^{25a} (Table II) describe the silicon atom as positively charged in every structure.^{25b} Nevertheless, group charges Q (computed for CH_3 or SiH_3 as sums of NAO atomic charges) show that the silyl group as a whole increases its electron density in going from the open chain to the cyclic structures 1d, 2a, and 2b ($\Delta Q = -0.199, -0.196,$ and -0.249 , respectively) about twice as much as methyl ($\Delta Q = -0.117$). In the case of silicon this increase occurs with almost equal contributions from the oxygen and CH_2 group; in the case of carbon the electron density increases not only on the methyl group but also on the oxygen atom (-0.141), at the expense of the CH_2 group. Dipole moments are reduced in going from the open-chain carbanions to the cyclic forms, in the case of silicon by more than 5 D and in the case of carbon by 1.7 D. Their orientations in the C and Si cyclic structures appear to be significantly different (Chart II, 6-31+G(d) dipole moments in D). Their

(24) (a) One might speculate that the solvent could generate a situation different from that described by the present computations, possibly stabilizing one or more structures with intermediate degrees of dissociation. The tighter of these noncompletely dissociated structures could have a character closer to that of a pair of radicals than to an ion pair. See, for instance, (b) pp 240–243. (b) Salem, L. *Electrons in Chemical Reactions*; Wiley: New York, 1982.

(25) (a) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* 1985, 83, 735–746. (b) The Si–H bonds are described as significantly polarized; for a discussion of bonding between silicon and hydrogen, carbon, oxygen, and fluorine, where polarization is analyzed in terms of basis set partitioning vs topological partitioning of the electron density, see: Gronert, S.; Glaser, R.; Streitwieser, A. *J. Am. Chem. Soc.* 1989, 111, 3111–3117.

Chart II

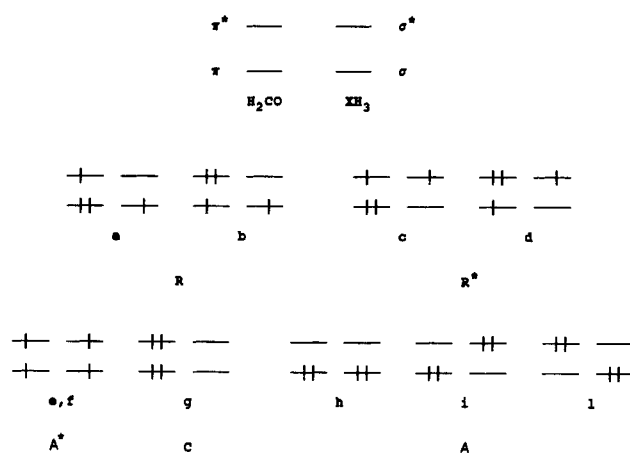


behavior seems to be consistent with the change in group charges just discussed, namely with a more substantial redistribution of the electron density on the silyl group than on methyl upon formation of a cyclic structure.

Both this redistribution and the geometrical features of the cyclic forms discussed above probably originate from the greater capability of silicon to engage in simultaneous bonding interactions with oxygen and carbon in the H_2CO group. Support for this assumption comes from the RHF/6-31+G(d) HOMO energy variation in going from the carbanions to the corresponding cyclic forms. The HOMO is initially more localized on the carbon atom bearing the formal -1 charge and becomes well delocalized over the whole system in the cyclic forms. The energy variation is opposite in the two cases: a sharp HOMO destabilization for carbon (MO eigenvalue from -0.047 in **3a** to -0.007 in **3b**) is contrasted by an equivalent stabilization found for silicon (MO eigenvalue from -0.074 in **1a** to -0.114 in **1d**, -0.123 in **2a**, and -0.128 in **2b**).

Qualitative CI Analysis. The significant differences in the energy profiles of the Wittig and Wright-West migrations (Figures 4 and 5, left sides) can be examined from another point of view by means of a qualitative study based on a limited configuration interaction.²⁶ For each critical point geometry, molecular orbitals localized on two fragments H_2CO and XH_3 ($\text{X} = \text{C}$ or Si) were obtained from MC-SCF computations²⁶ performed at large inter-fragment separation. These "separated fragment orbitals" were subsequently used (after reorthogonalization) in a series of CI calculations²⁵ performed at the original geometries.^{27,28} A minimal valence space was defined by choosing as active molecular orbitals the fragment orbitals most directly involved in bond breaking (or formation),

Chart III



and also considering the possibility (through the appropriate spin couplings) of simultaneous bonding interactions between the migrating center X and the two atoms C and O of the other fragment. The active orbitals include the quasi- π and quasi- π^* orbitals of the pyramidalized H_2CO fragment (with significant $2s$ components on carbon in all geometries but **1b**), and the σ and σ^* orbitals of the XH_3 fragment (the former is dominated by an sp hybrid on X pointing toward the H_2CO fragment; the latter has a dominant Si-H antibonding component). These orbitals are populated with four electrons in all possible ways: the resulting complete CI in the active space so defined consists of only 20 configurations. The more important of these are shown in Chart III. The letters R, A, and C, used to label them, stand for a radical, anionic, or cationic XH_3 fragment, respectively. These symbols are starred if the σ^* MO of the XH_3 fragment (rather than σ) is involved in spin coupling with the H_2CO fragment MO's.

The choice of active orbitals (all symmetric with respect to the COX plane) and the low symmetry of the two reaction paths, as defined by the critical points of Figures 1-3, imply a mixing of all configurations. Figure 6 shows the behavior of the lowest CI eigenvalues as a function of the methyl or silyl shift. The two energy curves corresponding to the lowest eigenvalue (representing in any

(26) Robb, M. A.; Eade, R. H. A. *NATO Adv. Study Inst. Ser., Ser. C* 1981, 67, 21-54. Hegarty, D.; Robb, M. A. *Mol. Phys.* 1979, 38, 1795-1812.

(27) Although the molecular orbitals so defined are very inadequate for a correct description of the system at bonding distances, they are useful for the purpose of a qualitative analysis.

(28) For each migration reaction the geometries of the critical points shown in Figures 1-3 have been used. Two additional noncritical points were added in the case of the carbon migration: the relevant geometries were obtained by optimization of all the geometrical parameters but the CCO or COC angles, which were held frozen at a value of 90° .

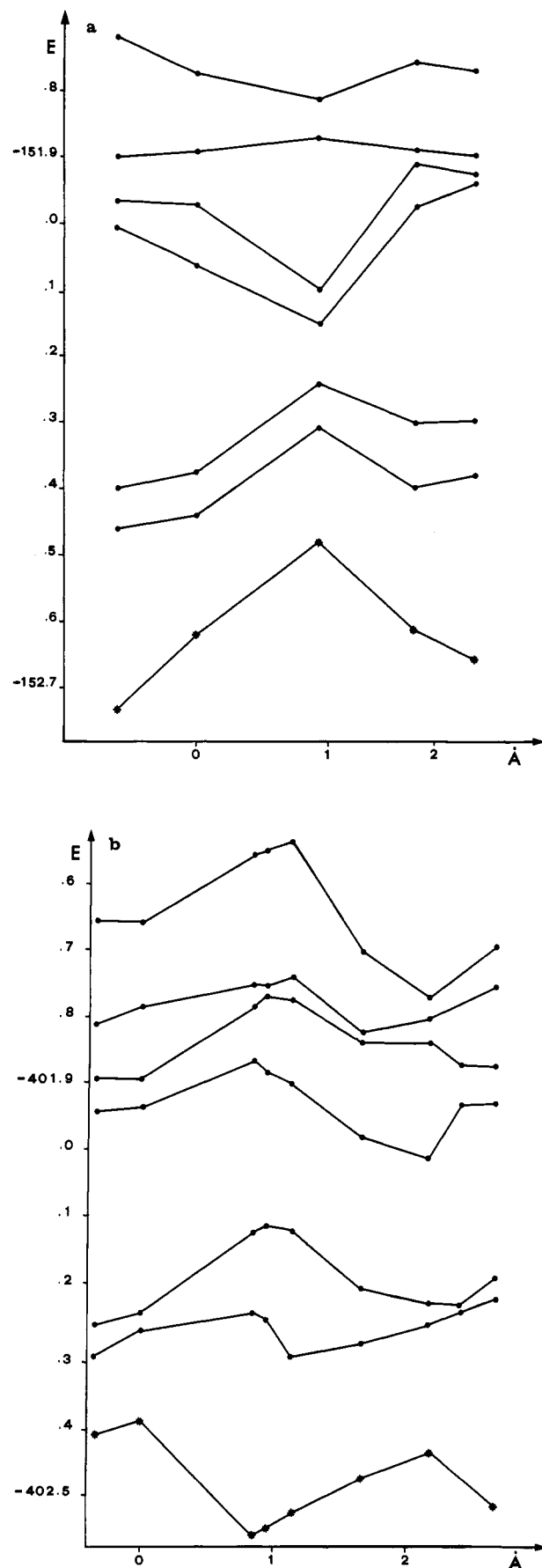


Figure 6. Avoided crossings in the energy profiles corresponding to the lowest CI eigenvalues: (a) Wittig migration; (b) Wright-West migration. Energies represented as a function of the carbon (a) or silicon (b) shift projected onto the C-O bond axis (origin in C, abscissa values in Å). The lowest curve (stars) was obtained by estimating the energy drop produced by orbital relaxation.

case arbitrary sections on the CI energy hypersurfaces) are expected to reproduce only in an approximate way the energy curves of Figures 4 and 5 (left) because the infinite separation orbitals are far from optimum at bonding distances. In the case of carbon (Figure 6a) two avoided crossings, involving mainly the four lowest states, occur in correspondence with the transition structure 3b, giving rise to energy maxima in the ground and first excited states. The third and fourth states show corresponding minima. In the ground-state eigenvector, configurations a and c carry more weight in the carbanionic and oxyanionic structures than in the corresponding cyclic transition structure, in which they lose importance. On the other hand, configurations b and d are more important in the cyclic structure than in the open ones.²⁹ In the transition structure, b is the dominant configuration, followed by the h and l configurations (A type), and then by d. The coefficients of configurations e and f (A* type) are small and almost constants for all geometries (they are, however, important configurations in the first excited state). "Closed shell" configurations of the A type are important in the central part of the energy profile in the case of carbon migration only, and not for silicon.

The energy profiles present a very different pattern in the case of silicon (Figure 6b). In the carbanion 1a the ground state is dominated by the a (R type) and d (R* type) configurations. By contrast, the first excited singlet is characterized by the c (R*) and b (R) configurations. At the geometry of the transition structure 1b an avoided crossing takes place, and the coefficients of configurations c and b grow in the ground state, while configuration a becomes more important in the first excited state. This avoided crossing appears to be the main feature of the first portion of the migration path, leading to the cyclic minimum 1d. The energy of the ground state is lowered as the avoided crossing occurs and drops even further in correspondence with 1d. A second interesting feature is that the weight of the A* configurations (present in both the ground and excited state of the carbanion) rises on going from the carbanion to the transition structure and then is lowered again when the system approaches the cyclic minimum geometry. In the cyclic structure 1d, R and R* configurations carry almost equal weights; for carbon, however, the R configuration b is much more important than the R* configuration d in 3b. Figure 7 emphasizes that the importance of configurations incorporating spin coupling between the two fragments with involvement of the σ^* orbital of the SiH₃ fragment grows on going from the open-chain silicon carbanion to the cyclic minimum.³⁰ This phenomenon does not occur for carbon.

The CI calculations discussed above allow us to also examine the nature of the barriers to dissociation for the two carbanions 1a and 3a. The fragment orbitals are used at every interfragment distance: by this procedure, the nature of the states that may be involved in the avoided crossing can be qualitatively assessed. Due to the low symmetry of the systems, many electronic states are allowed to "mix" when the two fragments are brought together; nevertheless, the origin of the barrier on the lowest energy curve can be traced back in a first approx-

(29) These configurations present a smaller electron repulsion, having the out-of-phase π^* orbital doubly occupied; this is accompanied by a larger overlap between the two spin-coupled orbitals.

(30) One reviewer has pointed out that the importance of σ^* orbitals as acceptors is well documented for transition metal complexes; for instance, in the case of phosphines, in: Marynick, D. S. *J. Am. Chem. Soc.* 1984, 105, 4064-4065. Xiao, S.-X.; Trogler, W. C.; Ellis, D. E.; Berkovitch-Yellin, Z. *J. Am. Chem. Soc.* 1983, 105, 7033-7037.

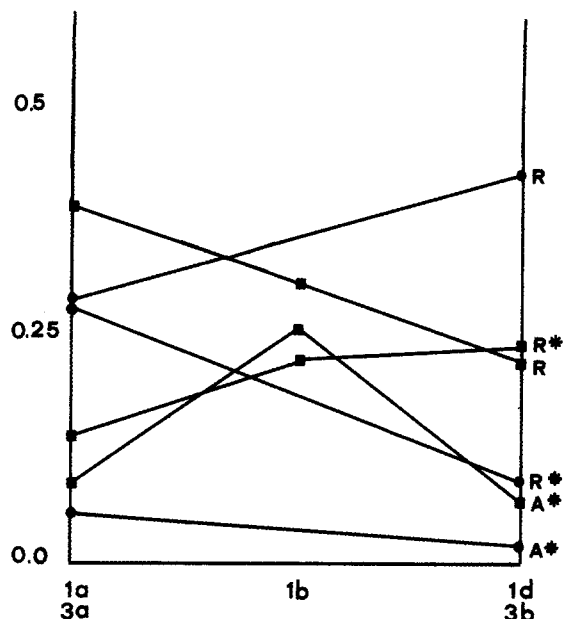


Figure 7. Weight variations (sum of squared coefficients) for groups of configurations in the ground-state CI eigenvector. Circles: Wittig migration. Squares: Wright-West migration.

imation to an avoided crossing^{24b} (occurring at an inter-fragment distance of approximately 3 Å) of the lowest CI root (1), dominated at large separation by the A configurations h, i, and l, with a state (2) characterized by R, R*, and A* configurations. At large separation the lowest state (1) corresponds to heterolytic dissociation, while the second low-energy state (2) corresponds to homolytic dissociation (configurations of the R and R* type). The third singlet state (3) is dominated at large separation by the two A* configurations; when the fragments get closer, it undergoes an avoided crossing with the fourth state (4) (R and R* configurations again) and is significantly stabilized and then rises in energy at closer distances. Then, at less than 3 Å, the A* configurations also appear in the ground-state eigenvector with non-negligible coefficients. Therefore, the R, R*, and A* configurations (together with another ionic contribution from configuration g, C type) make important contributions to the description of the incipient bonding in the carbanion. On the other hand, the A configurations, which dominate the lowest solution at large separation (1), are repulsive in nature and contribute, at bonding distances, to states that are higher in energy. These features are common to the two carbanions 1a and 3a. The avoided crossing between the CI roots (1) and (2) then lies at the origin of the barriers to dissociation.

Conclusions

In the case of silicon, the model direct [1,2] migration has been found to take place in two kinetic steps, passing

through a strained cyclic intermediate in which silicon is pentacoordinate. Both these steps present low activation energy barriers. On the other hand, the model carbon [1,2] migration goes through a single transition structure, and, although very exothermic, faces a significantly higher energy barrier. A dissociative process has also been considered for the carbon and silicon carbanions 1a and 3a, with the purpose of assessing, in the case of silicon, if the migration process can be considered a realistic path toward the oxyanion. A study of the methyl and silyl dissociation processes in 1a and 2a shows that the former is preferred over the model methyl [1,2] shift, while the barrier for the latter is much higher than those for silyl [1,2] migration. These computational data indicate completely different mechanisms for the formally similar Wright-West and Wittig migrations.

The remarkable differences between the two reaction energy profiles lie in the existence of the silicon pentacoordinate intermediate, which is stable, notwithstanding the strain in the cyclic structure. An analysis of the geometrical features of the carbon and silicon cyclic structures and of their electron density distributions allows us to trace back this stability to the greater ability of the silyl group to participate in bonding interactions with the H₂CO group. These interactions allow a partial redistribution of the electron density away from the H₂CO part of the molecule as a cyclic structure is formed. A qualitative CI analysis in terms of fragment orbitals indicates that the intervention of an antibonding SiH₃ orbital is crucial in determining this bonding capability. An important difference between the carbon and silicon migrations appears to be the occurrence of an avoided crossing for the latter in correspondence with the transition structure 1b: a configuration dominating the first excited singlet in the carbanion 1a and incorporating spin coupling between the π* orbital of the H₂CO fragment and the σ* SiH₃ orbital becomes very important when the system gets closer to the cyclic structure. In the cyclic structures the roles of configurations involving the σ* XH₃ orbital is significant for silicon but not for carbon.

Although in the present paper neither the role of the counterion nor solvent effects have been taken into account, both the different shapes of the energy profiles for the migration processes and the comparison of the migration energy barriers with the estimated barrier heights for the dissociative processes allow the conclusion that the probable mechanism of the Wright-West migration lies in sharp contrast with that accepted for the Wittig rearrangement.

Acknowledgment. This work was partially supported by the Ministero della Ricerca Scientifica e Tecnologica, the Italian C.N.R., and by a computational grant from CSI-Piemonte.