7066 J. Org. Chem. 1996, 61, 7066−7076

Regioselectivity Patterns Featured by Formaldehyde in the Electrophilic Addition to *gem*-Difluoro and *gem*-Dichloroallyl Systems. An ab Initio Theoretical Study

Carlo Canepa and Glauco Tonachini*

Dipartimento di Chimica Generale e Organica Applicata dell' Università di Torino,
Corso Massimo D'Azeglio, 48 10125 Torino, Italy

Received September 5, 1995 (Revised Manuscript Received June 20, 1996[⊗]*)*

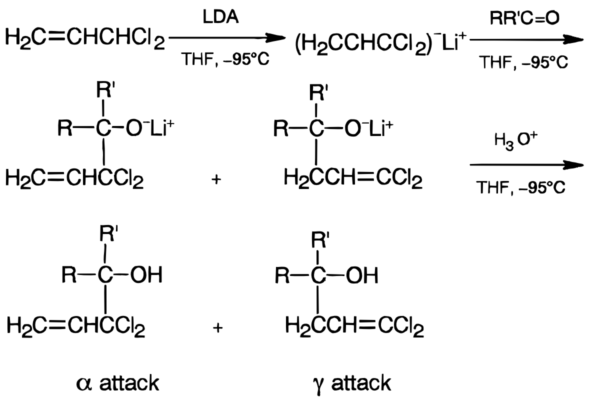
The addition reactions of formaldehyde with (1,1-difluoroallyl)lithium and (1,1-dichloroallyl)lithium and -potassium (and corresponding free anions) have been investigated at the HF and MP2 levels of theory. The two competing pathways leading from the initial electrostatic σ-complexes to the α and γ addition products have been studied. In (1,1-difluoroallyl)lithium, (1,1-dichloroallyl)potassium, and both free anions the α-pathway is sharply preferred. In contrast, for (1,1-dichloroallyl)lithium the difference between the two activation energies is smaller and in favor of the γ-pathway: as a consequence, on the basis of the present calculations, it is expected that in this case varying substituents on the electrophilic carbon could modulate the regioselective preferences. All results appear to be consistent with available experimental evidences. A balance between an exothermicity factor and the different destabilization undergone by the various reactants in the transition structures offers a qualitative rationalization of the opposite regioselective inclinations of (1,1-dichloroallyl)lithium with respect to the other systems.

Introduction

gem-Dihalo allyl anions are potentially ambident nucleophilic species, whose regioselective behavior was first investigated by Seyferth and co-workers.[1] For instance, experiments carried out on a large number of different carbonyl electrophiles showed a variable preference for the disubstituted (α) or the unsubstituted (γ) terminus of the lithium *gem*-dichloroallyl system (a typical experiment on this species is outlined in Scheme 1). In contrast, the similar *gem*-difluoroallyl system invariably displayed a complete α-selectivity.[1e]

Further regioselectivity studies, carried out in this laboratory on the *gem*-dichloroallyl system, revealed that it depends also on (i) the nature of the counterion (the susceptivity of the α terminus toward electrophilic attack increases in the series Li, Na, K); (ii) the degree of interaction of the cation with the anionic system (for instance, the presence of 12-crown-4 shifts the regioselectivity of (1,1-dichloroallyl)lithium toward the α terminus).[2] In related theoretical studies we investigated some structural and electronic features of *gem*-dihaloallyl anions, considering their association with an alkali-metal counterion, with the purpose of attempting an interpretation of their regiochemistry, and, in the case of the relevant monosubstituted systems, a prediction of the regiochemical preferences.[2] For these systems, several stable structures were determined computationally. In a few of these, the counterion is found in a bridging position between the α and γ carbons (as is the case of the parent allyllithium system).[3] In other structures, which come out to be more stable, the cation interacts only with the substituted carbon and one or two halogen atoms. The preference for unbridged structures is more distinct in the case of the lithium difluoro system,[2a] while in the dichloro systems the bridged ("internal" Li^+) and unbridged ("external" Li^+) structures are closer in energy.[2c] In the case of (1,1-dichloroallyl)lithium the internal structure is less stable by ca. 4 kcal mol^{-1}; for Na and K this energy difference is ca. 6 kcal mol^{-1}, but the internal structure is more asymmetric, and the cation cannot be considered as interacting with the γ carbon to the same extent to which it interacts with the α carbon.[2c]

Scheme 1



The study of the reaction of formaldehyde with the metalated 1,1-dihaloallyl systems (reaction 1, Scheme 2), as well as with the corresponding anions (reaction 2, Scheme 2), is expected to provide a verification of the

---

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

(1) (a) Seyferth, D.; Mammarella, R. E.; Klein, H. A. *J. Organomet. Chem.* **1980**, *194*, 1. (b) Seyferth, D.; Murphy, G. J.; Mauzé, B. *J. Am. Chem. Soc.* **1977**, *99*, 5317. (c) Seyferth, D.; Murphy, G. J.; Woodruff, R. A. *J. Organomet. Chem.* **1974**, *66*, C29. (d) Seyferth, D.; Murphy, G. J.; Woodruff, R. A. *J. Am. Chem. Soc.* **1974**, *96*, 5011. (e) Seyferth, D.; Simon, R. N.; Sepelak, D. J.; Klein, H. A. *J. Am. Chem. Soc.* **1983**, *105*, 4634.

(2) (a) Tonachini, G.; Canepa, C. *Tetrahedron* **1989**, *45*, 5163. (b) Angeletti, A.; Baima, R.; Canepa, C.; Degani, I.; Tonachini, G.; Venturello, P. *Tetrahedron* **1989**, *45*, 7827. (c) Canepa, C.; Tonachini, G.; Venturello, P. *Tetrahedron* **1991**, *47*, 8739. (d) Canepa, C.; Prandi, C.; Tonachini, G.; Venturello, P. *Trends Org. Chem.* **1993**, *4*, 535−553. (e) Canepa, C.; Cobianco, S.; Degani, I.; Gatti, A.; Venturello, P. *Tetrahedron* **1991**, *47*, 1485.

(3) Bongini, A.; Cainelli, G.; Cardillo, G.; Palmieri, P.; Umani-Ronchi, A. *J. Organomet. Chem.* **1976**, *110*, 1. Clark, T.; Jemmis, E. D.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A. *J. Organomet. Chem.* **1978**, *150*, 1. Neugebauer, W.; Schleyer, P. v. R. *J. Organomet. Chem.* **1980**, *198*, C1. Decher, G.; Boche, G. *J. Organomet. Chem.* **1983**, *259*, 31. Schleyer, P. v. R. *J. Am. Chem. Soc.* **1985**, *107*, 4793. Winchester, W. R.; Bauer, W.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1987**, 177.

S0022-3263(95)01620-3 CCC: $12.00

Scheme 2

$$H_2C{=}O + M^+(H_2C\text{-}CH\text{-}CX_2)^- \longrightarrow$$
$$H_2C{=}CH\text{-}CX_2\text{-}CH_2\text{-}O^-M^+ + X_2C{=}CH\text{-}CH_2\text{-}CH_2\text{-}O^-M^+ \quad (1)$$

$$H_2C{=}O + (H_2C\text{-}CH\text{-}CX_2)^- \longrightarrow$$
$$H_2C{=}CH\text{-}CX_2\text{-}CH_2\text{-}O^- + X_2C{=}CH\text{-}CH_2\text{-}CH_2\text{-}O^- \quad (2)$$

(a: X=F, M=Li; b: X=Cl, M=Li, K)

conclusions previously drawn on the only basis of the features of the reactants.

Indeed, the study of these simple reactions can in principle indicate an “intrinsic” inclination of the fluoro or chloro allylic systems toward α or γ selectivity with respect to the carbonyl carbon, and the dependence, if any, of this property from the presence of the alkali metal counterion. Thus, a base-line for further investigations on more complex aldehydes will be available.

In two previous studies[4] we have attempted to assess the inclination of lithium and sodium *gem*-difluoro and -dichloro systems toward dimerization. Contrasting results were obtained for the two different substitutions, in that difluoro systems were described as showing a clear preference for dimeric structures, favored by the entropy contribution, while in dichloro systems the energy term was dominating, and the equilibrium was shifted in favor of the monomeric species (this preference was set in a more clearcut way in the case of a lithium counterion). In the present study the reactivity of dimeric species is not examined: due to this limitation, the results pertaining to the difluoroallylic systems have to be interpreted with some caution. In a subsequent study the influence of solvation effects on the description of these reactions will be explored.[5]

Method

The study of the addition reactions was performed by determining, on the relevant energy hypersurfaces, the critical points corresponding to stable and transition structures. This was initially accomplished by way of complete gradient optimization[6] of the geometrical parameters at the Hartree−Fock (HF) level of theory, using the split-valence shell 3-21G(*) basis set[7a] (with d polarization functions only on chlorine). Diffuse sp functions were also added to this basis set in the case of anionic species. The critical points were characterized as minima or first-order saddle points through diagonalization of the analytically calculated Hessian matrix (vibrational frequencies calculation). Right from the onset, the results obtained at the monodeterminantal level of theory in the case of the first γ transition structure (see below) were checked by redetermining the optimum structure by complete active space (CAS) MC-SCF calculations[8] (six electrons in five orbitals define the active space, in which a full CI is performed; further details will be provided in the following section). Having assessed that the monodeterminantal description was qualitatively reliable, we redetermined the critical point geometries in the following, by introducing correlation effects through perturbative MP2 computations,[9] in conjunction with the same basis sets used in the previous calculations. The MP2/3-21G(*) geometries were then used for recomputing the energy barriers at the MP2/6-31G(d) level. In one case, (difluoroallyl)lithium, it was possible to calibrate the level of theory used throughout, by carrying out MP2 optimizations with the 6-31G(d) and 6-31+G(d) basis sets[7b] (the latter contains d polarization functions, as the former, and diffuse sp functions on all non-hydrogen atoms). The agreement between the two sets of calculations was found to be acceptable (see the Appendix). The GAUSSIAN92 system of programs[10] was used throughout, on an IBM RISC/6000-550.

Results and Discussion

Addition Reaction of Formaldehyde to (1,1-Dichloroallyl)lithium. The geometries of the two more stable structures of the reactant nucleophile are reported in ref 2c (Figures 2c and 2d). The more stable is open-chain, with lithium bound to the substituted terminus, which is significantly pyramidalized ($\tau = 148°$);[11] the two C−C bond lengths, which approximate the typical values found for single and double CC bonds at this level of calculation,[12] differ by 0.16 Å. The less stable one is a lithium-bridged structure, in which the two C−C bond lengths differ by 0.09 Å only; thus, the CCC skeleton part more closely resembles a π-delocalized allylic system ($\tau = 131°$). The stability of these structures is comparable, their energies differing by less than 4 kcal mol^{-1}. However, only one σ-complex between formaldehyde and (1,1-dichloroallyl)lithium was found in the present study (Figure 1a). Any attempt to locate a lithium-bridged complex failed, and the optimizations converged on **1a**, in which lithium interacts with the α terminus only. No energy barrier was found to separate the reagents from this minimum.

The description of this first part of the reaction pathway (from the two separate reagents to the σ-complex) can be deemed to be significantly different in solution. Ether solvents, which are generally used in the experiments, interact significantly with the cation and would compete with the allylic halogens in this respect. In particular, to allow the formation of the ion−dipole complex, a solvent molecule among those surrounding the cation is to be displaced by the incoming electrophile, and the solvent itself has to undergo some reorganization. In

---

[4] Canepa, C.; Antoniotti, P.; Tonachini, G. *Tetrahedron* **1994**, *50*, 8073−8084. Canepa, C.; Tonachini, G. *Tetrahedron* **1994**, *50*, 12511−12520.

[5] Canepa, C.; Tonachini, G. To be published.

[6] Schlegel, H. B. In *Computational Theoretical Organic Chemistry*; Csizsmadia, I. G., Daudel, R., Eds.; Reidel Publ. Co.: Dordrecht, The Netherlands, 1981; p 129. Schlegel, H. B. *J. Chem. Phys.* **1982**, *77*, 3676; Schlegel, H. B.; Binkley, J. S.; Pople, J. A. *J. Chem. Phys.* **1984**, *80*, 1976. Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214.

[7] (a) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. (b) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724−728. Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213−222.

[8] Robb, M. A.; Eade, R. H. A. *NATO ASI Ser. C* **1981**, *C67*, 21.

[9] (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Binkley, J. S.; Pople, J. A. *Int. J. Quantum Chem.* **1975**, *9*, 229.

[10] Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Ragavachari, K.; Binkley, J. S.; Gonzales, C.; Martin, R. I.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian Inc., Pittsburgh, PA, 1992 (GAUSSIAN92).

[11] The pyramidalization angle τ is defined as the angle between the normal to the CX_2 plane and the $C\alpha C\beta$ bond: therefore, a planar structure has $\tau = 90°$, while a tetrahedral arrangement corresponds to $\tau = 144.7°$.

[12] Compare for instance the carbon−carbon bond lengths in propene, which are, at the HF/3-21G computational level, 1.510 Å (C−C) and 1.316 Å (C=C).

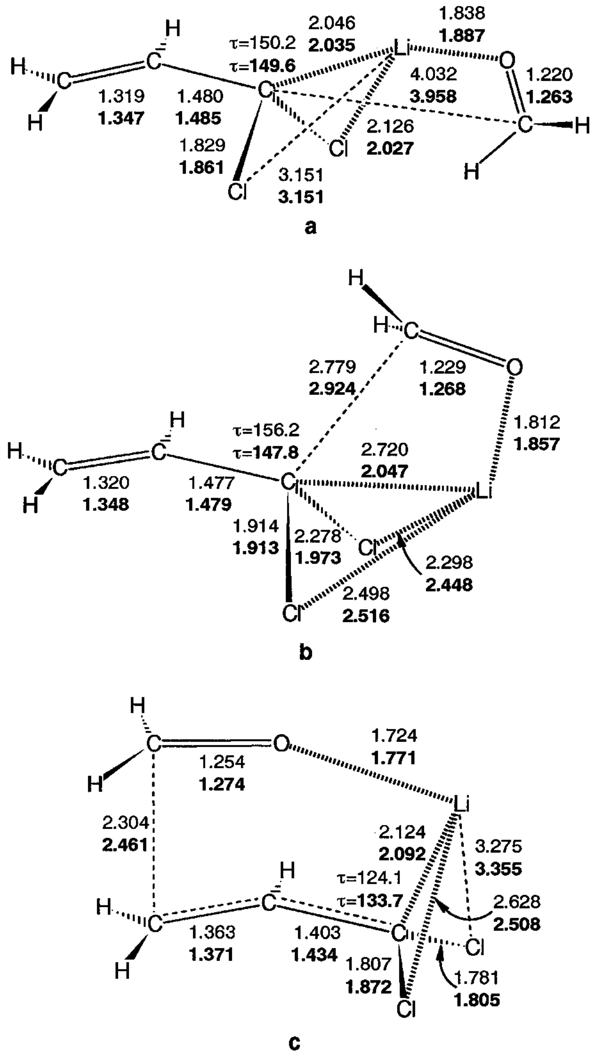


Figure 1. (a) The σ-complex between formaldehyde and (1,1-dichloroallyl)lithium; (b) the α-transition structure; (c) the γ-transition structure. Interatomic distances in angstroms, angles in degrees (plain figures: HF; bold: MP2).

this study, the attention focuses on the possible differences between the α and γ attacks which can originate from the ion−dipole complex itself: it has thus been tentatively assumed that in the electrostatic complex and in the two following transition structures (see below) the coordination of lithium would not be inclined to undergo significant modifications. In all structures lithium could directly engage two oxygenated solvent molecules, while simultaneously maintaining its interaction with the carbonyl oxygen and the anionic allylic moiety. However, it must be admitted that solvation effects might bring about a reduced interaction between the cation and the halogens: this would happen in both the complexes and transition structures, but could in turn affect to some extent the description of the regioselective behavior. The assessment of the importance of this point (which is beyond the scope of the present paper) will be addressed in a subsequent study.[5]

Two transition structures connect the σ-complex to the α and γ products: these are shown in Figures 1b and 1c, respectively. The geometrical changes taking place along the two alternative pathways are very different. In the α attack the vinylic part of the nucleophile is not involved in the formation of new bonds: it can be observed that in **1b** the C_α−C_β and C_β−C_γ bond lengths have changed very little from their values in **1a**. In contrast, in the transition structure **1c** for the γ attack the two C−C bond lengths have less different values, and the pyramidalization angle (τ) value has dropped significantly (the τ parameter shows some dependence on the computational level). Considering the length of the new C−C bond in formation, the α transition structure, **1b**, can be viewed as "earlier" than the γ, **1c** (O−Li bond lengths vary consistently, considering that at the end of the reaction a lithiated oxyanion is obtained). The energy barriers (Table 1) show some preference for the γ pathway, but are not very different. This description seems to be in accord with the available experimental data, which show a variable regioselectivity, depending on the substituents on the carbonyl carbon (experimental data relevant to H_2CO itself seem, to our knowledge, not to be available). Both reactions are exothermic, the α addition slightly more so (α and γ addition products are not shown; energies are reported in Table 1).

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

structure		MP2/3-21G(*)[c] E	MP2/3-21G(*)[c] Δ*E*	RHF/3-21G(*)[c] E	RHF/3-21G(*)[c] Δ*E*
		(1,1-Dichloroallyl)lithium			
σ-complex	**1a**	−1150.945458	0.0	−1150.154966	0.0
α T. S.	**1b**	−1150.930937	9.1	−1150.137338	11.1
γ T. S.	**1c**	−1150.937653	4.9	−1150.140913	8.8
α product	–	−1150.981667	−22.7	−1150.190488	−22.3
γ product	–	−1150.975646	−18.9	−1150.186707	−19.9
		(1,1-Difluoroallyl)lithium			
σ-complex	**2a**	−433.912393	0.0	−433.175888	0.0
α T. S.	**2b**	−433.906413	3.8	−433.169962	3.7
γ T. S.	**2c**	−433.888172	15.2	−433.143535	20.3
α product	–	−433.955071	−26.8	−433.224341	−30.4
γ product	–	−433.945254	−20.6	−433.210459	−21.7
		(1,1-Dichloroallyl)potassium			
σ-complex	**5a**	−1739.482037	0.0	−1738.706385	0.0
α T. S.	**5b**	−1739.476240	3.6	−1738.701976	2.8
γ T. S.	**5c**	−1739.471075	6.9	−1738.687194	12.0
α product	–	−1739.502494	−12.8	−1738.726552	−12.7
γ product	–	−1739.484022	−1.2	−1738.712854	−4.1

[a] Hartrees. [b] kcal mol^{-1}. [c] Level of theory at which the geometries of the critical points were optimized.

Before proceeding with the redetermination of the reaction profile at the MP2 perturbative level, a test was carried out on the γ transition structure at the CAS-MCSCF level of theory (with the 3-21G(*) basis set) with the purpose of assessing if the monodeterminantal description of the wavefunction is qualitatively correct. In order to describe the formation and disruption of σ and π bonds in an equilibrate manner, the following valence orbitals of the reactants were chosen as active orbitals in these computations: two allylic orbitals dominated by the π and π* couple of the C_β−C_γ bond; another allylic orbital dominated by an sp hybrid located on C_α, pointing toward lithium (these are equivalent to the three π orbitals of a planar allylic system) and, finally, the π and π* couple of the carbonyl electrophile. On the basis of preliminary test calculations, lithium was considered to interact mostly in an electrostatic way with the O and C_α centers; therefore neither its empty orbitals nor the oxygen lone pairs were included in the active space. A full CI was then performed within this active space, and the molecular orbitals were allowed to relax, to obtain MCSCF wavefunction and energy. The transition structure was reoptimized at this level of theory. The length of the forming CC bond is the parameter more sensitive to the change in computational level, being longer by ca.

0.09 Å in the MCSCF structure; the angles do not show large variations. The primary result is, however, that no diradical character is detected in the wavefunction relevant to the critical point. In conclusion, it seems to be adequately described at the monodeterminantal level of theory.

The results of this test allowed us to safely proceed with the reoptimization of the geometries of the σ-complex and of the two transition structures at the MP2/3-21G(*) level, in order to estimate the effect of electron correlation on the description of the two reaction pathways. In order to calibrate this theory level, further tests on the extension of the basis set at the MP2 level (affordable only for the smaller lithium difluoro system) were carried out and provided encouraging results (see next subsection and the Appendix for details). The optimum MP2/3-21G(*) geometrical parameters are reported again in Figure 1 (bold figures), and the relevant energies and energy differences in Table 1. Almost all bond lengths are longer than the corresponding HF bond lengths (compare for instance the $C_\alpha{-}C_\beta$ and $C_\beta{-}C_\gamma$ distances). The C(aldehyde)$-C_\alpha$ distance in the α transition structure, and the C(aldehyde)$-C_\gamma$ distance in the γ transition structure, are both longer by 0.14 Å, and by 0.16 Å, respectively. Therefore, the two transition structures appear to be described, as slightly earlier, in a geometrical sense. The remaining parameters do not show significant variations. For the dichloro system, both energy barriers are lower than those computed at the HF level. The preference for the γ-pathway is enhanced, the α barrier being larger by ca. 4 kcal mol^{-1} at the MP2 level (the difference was ca. 2 kcal mol^{-1} at the HF level). MP2/6-31G(d) single-point energy calculations (performed using the MP2/3-21G(*) geometries just discussed) further lower the estimate of the activation energies, while keeping the difference between the two pathways: the α barrier is computed to be 4.8 kcal mol^{-1}, and the γ barrier is reduced to just 1.3 kcal mol^{-1}. However, it must be kept in mind, when considering these figures, that carrying out single-point energy calculations, althought a common procedure, actually probes in an arbitrary way the higher-level energy hypersurface.

Addition Reaction of Formaldehyde to (1,1-Difluoroallyl)lithium. The HF geometries of the two more stable structures of the reactant nucleophile are reported in ref 2a (Figures 2f and 2g). In contrast with the results obtained for the similar dichloro system, both are open-chain structures (of similar stability) in which lithium interacts with the α carbon and one fluorine atom; both are significantly pyramidalized.[11] However, the actual starting point for the two alternative pathways to be considered here is again an ion–dipole complex between the reactants, which corresponds to a stable minimum (intermediate) on the energy surface. The optimum geometry of such a σ-complex, in which the two moieties interact electrostatically through the carbonyl oxygen and the lithium cation, is shown in Figure 2a; the HF structure appears to be similar to the one found for the dichloro system, **1a**. Its formation is described as taking place without any energy barrier.

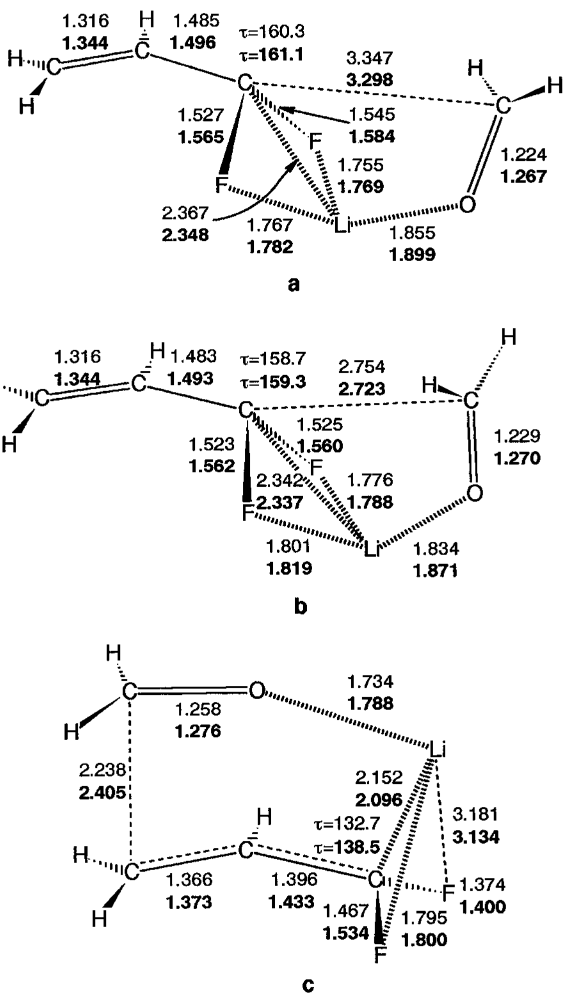


Figure 2. (a) The σ-complex between formaldehyde and (1,1-difluoroallyl)lithium; (b) the α-transition structure; (c) the γ-transition structure. Interatomic distances in angstroms, angles in degrees (plain figures: HF; bold: MP2).

The α and γ HF transition structures are shown in Figures 2b and 2c, respectively. As was the case for the dichloro system, the "reactant" σ-complex undergoes quite different geometrical changes in the two cases. Thus, in the transition structure **2b** the $C_\alpha{-}C_\beta$ and $C_\beta{-}C_\gamma$ bond lengths, as well as the τ angle, have virtually unmodified values, which approximate the usual values of single and double CC bonds at this computational level.[12] On the other hand, because of the involvement of the vinylic part of the nucleophile in the γ attack, the transition structure **2c** has two CC bonds of similar length, and the τ angle value is significantly reduced. The $C_\alpha C_\beta$ bond is undergoing a contraction, while the $C_\beta C_\gamma$ bond is stretched (these will end up being, in the γ product, a double and single bond, respectively). Comparing the two interatomic distances relevant to the new CC bond in formation, the α transition structure, **2b**, can be thought of as being "earlier" than the γ, **2c**. O–Li bond lengths vary consistently. This result closely parallels that obtained for the dichloro system. On the other hand, the result relevant to the height of the two energy barriers is in sharp contrast with the previous case: indeed, the data reported in Table 1 show that the α-pathway is by far preferred over the γ. This finding is in accord with the available experimental data: in fact, (*gem*-difluoroallyl)lithium shows a complete α-selectivity.[1e] The two reaction pathways, leading to the α and γ addition products (whose geometries are not shown), also exhibit a different exothermicity, with the former product more stable by ca. 8 kcal mol^{-1} (Table 1).

As done before for the analogous dichloro system, the geometries of the σ-complex and of the two transition structures were reoptimized at the MP2 level (using the

Table 2. Free Anions. Total[a] and Relative[b] Energies of the Critical Points

structure		MP2/3-21+G(*)[c] E	MP2/3-21+G(*)[c] ΔE	RHF/3-21+G(*)[c] E	RHF/3-21+G(*)[c] ΔE
		1,1-Dichloroallyl			
electrostatic complex	**3a**	(−1143.554965)	0.0	−1142.740144	0.0
α T. S.	**3b**	(−1143.554965)	(0.0)	−1142.738920	0.8
γ T. S.	**3c**	−1143.550307	2.9	−1142.725514	9.2
α product	–	−1143.591446	−22.9	−1142.769598	−18.5
γ product	–	−1143.568073	−8.2	−1142.751394	−7.1
		1,1-Difluoroallyl			
electrostatic complex	**4a**	−426.569643	0.0	−425.790572	0.0
α T. S.	**4b**	−426.568776	0.5	−425.787172	2.1
γ T. S.	**4c**	−426.558535	7.0	−425.762488	17.6
α product	–	−426.613948	−27.8	−425.835333	−28.1
γ product	–	−426.582238	−7.9	−425.800414	−6.2

[a] Hartrees. [b] kcal mol^{-1}. Figures in parentheses refer to a shoulder zone (see text). [c] Level of theory at which the geometries of the critical points were optimized.

same basis set); the optimum geometrical parameters are reported again in Figure 2, and the relevant energy data in Table 1. As observed for the analogous dichloro structures, the $C_\alpha-C_\beta$ and $C_\beta-C_\gamma$ bond lengths are consistently longer with respect to the HF values. The C(aldehyde)$-C_\alpha$ distance in the α transition structure is slightly shorter (−0.03 Å), while the C(aldehyde)$-C_\gamma$ distance in the γ transition structure is longer by 0.17 Å. The remaining parameters do not show significant variations. The preference for the α-pathway is maintained, although the γ barrier is significantly lowered. MP2/6-31G(d) single-point energy calculations (performed using the MP2/3-21G(*) geometries) further lower the estimate of the activation energies: the α barrier is computed to be 1.5 kcal mol^{-1}, and the γ barrier is reduced to 6.1 kcal mol^{-1}. This kind of computation should in general be considered with some caution, as remarked above for the lithium dichloro system. However, on the smaller difluoro system, it was possible to carry out a computational test, which allowed us to address three different aspects of the level of calculation used throughout this study. The first point is the degree of reliability of the results of MP2 optimizations uniformly conducted with the rather modest 3-21G(*) basis set. The second aspect regards the confidence that can be placed in the single-point MP2/6-31G(d) energy calculations just mentioned. The third one makes reference to the use of diffuse functions, introduced in the free anions (see below) but not used for the three metalated systems: is it legitimate to drop these functions as not important in the neutral systems? To assess these points, two sets of optimizations were then carried out, at the MP2/6-31G(d) and 6-31+G(d) computational levels, on the structures **2a**, **2b**, and **2c**. The results so obtained can be deemed to validate, at least qualitatively, those collected at the lower computational level (the same barrier ordering is found, although the γ barrier is more significantly lowered than the α). The tests also give a positive answer to the other two questions. Details on the optimum geometrical parameters and the energetics are discussed in the Appendix.

Addition Reaction of Formaldehyde to 1,1-Difluoro- and Dichloroallyl Anions. The reactions described in the two preceding subsections correspond to an extreme situation of tight interaction of the cation with the two reacting molecules. The study of the free anion reactions provides another extreme picture, in which this interaction is absent, and is expected to allow as a consequence a better understanding of the role of the counterion in affecting the chemical behavior of the reacting molecules. For the free anion reactions three sets of structure optimizations were carried out: (i) at the HF/3-21G(*) level (the optimum geometries reported in Figures 3 and 4, plain figures, are directly comparable with those of the preceding subsection); (ii) at the same theory level but using the 3-21+G(*) basis set, augmented by diffuse functions on all non-hydrogen atoms (figures marked with a +); (iii) at the MP2/3-21+G(*) level (bold figures). The energies and energy differences of the critical points are reported in Table 2, only for the computations with diffuse functions. Ion−dipole complexes are found also in the absence of a counterion (indeed, electrostatic complexes of this kind are expected when studying gas-phase models of ionic reactions). In the case of the free anions the interaction which keeps together the two moieties involves the formaldehyde hydrogens and the α terminus of the allylic system.

Dichloroallyl Anion. The optimum geometry of the complex in the dichloro case has a carbonyl $C-C_\alpha$ distance larger than 3 Å, and also the aldehyde hydrogens and the two chlorine atoms are ca. 3 Å apart (Figure 3a). At the HF level, the α transition structure (Figure 3b) is barely higher in energy than the complex, while the γ transition structure (Figure 3c) is more than 8 kcal mol^{-1} higher; the former is also earlier, in a geometrical sense. The small α energy barrier (which contrasts that found for the lithiated system) even desappears at the MP2 level. In this case, when searching for the α transition structure, only a “shoulder” zone is found (energy gradient very close to zero), approximately in correspondence of the HF ion−dipole complex structure; consequently, the corresponding geometrical parameters are reported in Figure 3a, while in Figure 3b no MP2 parameters are inscribed. Therefore, the complex does not appear to be a stable structure on the MP2 surface, because the pathway to the α product is all downhill: this result sharply contrasts the 9 kcal mol^{-1} barrier found in correspondence to the lithiated α transition structure (Table 1). Interestingly, the results for the α and γ pathways provide two divergent comparisons with the lithiated systems. Indeed, a MP2 γ transition structure is still found, located at less than 3 kcal mol^{-1} above the shoulder zone (2 kcal mol^{-1} lower than in the lithiated compound). The estimate for the γ barrier at both computational levels is much closer to that obtained for the lithiated system. These results suggest that the origin of the α barrier is associated to the presence of the counterion, while the γ barrier (although lower for the free anion) appears to be more strictly related to the structural changes of the allylic skeleton. The HF α

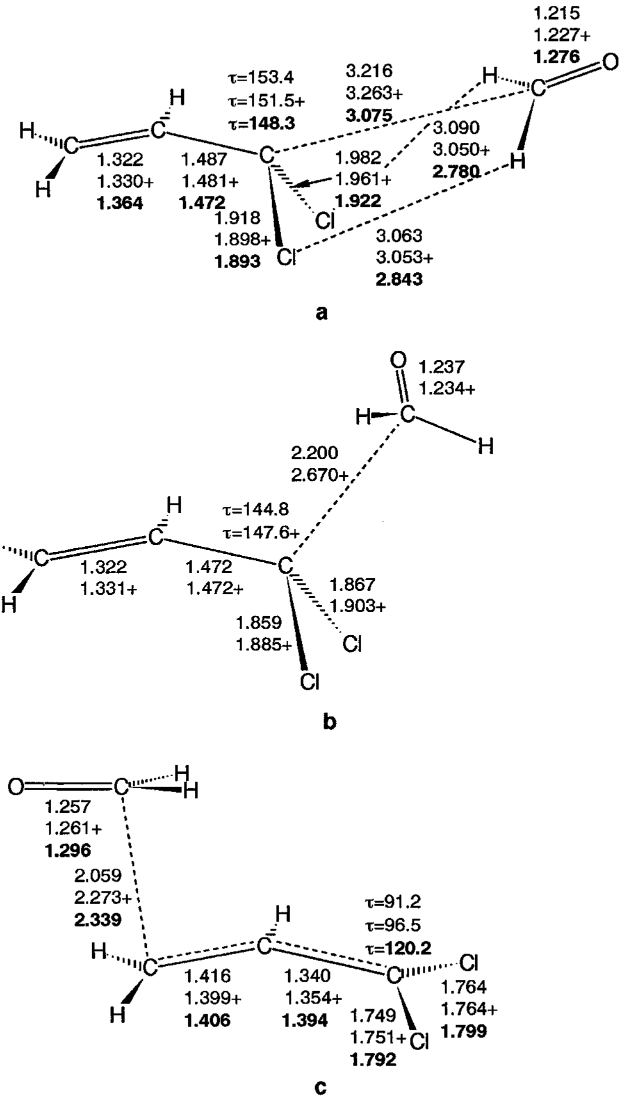


Figure 3. (a) The ion−dipole complex between formaldehyde and the 1,1-dichloroallyl anion; (b) the α-transition structure; (c) the γ-transition structure. Interatomic distances in angstroms, angles in degrees (plain figures: HF; marked with a +: with diffuse functions; bold: MP2).

transition structure **3b** occurs significantly later, in a geometrical sense, than in the case of the lithiated system. Comparing for instance the HF/3-21G(*) values, we observe that the C−C$_\alpha$ distance is 0.58 Å shorter than in **1b**, while the aldehydic CO bond is 0.01 Å longer. The same is true for the γ transition structure **3c**: its later occurrence with respect to **1c** is reflected by all of the interatomic distances between the carbons involved in bond reorganization. Thus, the C−C$_\gamma$ distance is shorter by 0.24 Å with respect to the value found in **1c**, while the C$_\alpha$−C$_\beta$ and C$_\beta$−C$_\gamma$ bond lengths are 0.06 Å shorter and 0.06 Å longer, respectively, than those optimized in **1c** (the former is becoming a double bond, and the latter a single bond). The τ angle value in **3c** depends on the level of theory to a significant extent. In conclusion, both these anionic transition structures are later, in a geometrical sense, than their counterparts in the lithiated system, and the α transition structure is earlier than the γ.

Difluoroallyl Anion. Also in the difluoro case an ion−dipole complex is found, held together by the interaction of the CF$_2$ group with the aldehydic hydrogens (Figure 4a). In this case the orientation of the two moieties comes out to be different with respect to **3a**, and the carbonyl C−C$_\alpha$ distance is longer. The α transition structure (Figure 4b) is located 2 kcal mol^{-1} above the complex (at the HF level), while the γ (Figure 4c) is higher by more than 15 kcal mol^{-1}. If the intercarbon distances of the bonds being formed are compared, the former appears to be earlier, as was the case for both the dichloro anion and the lithiated difluoro compound. Table 2 shows that the MP2 calculations lower significantly both barrier values (while little affecting the exothermicity): the α barrier is less than 1 kcal mol^{-1}, and this pathway is clearly preferred, as was the case for the lithiated systems. Comparing the fluorinated anion with its lithiated counterpart, we can see that lithium raises both barriers, more so the γ, and consequently the preference for the α pathway is kept: this result contrasts that relevant to the dichloro systems. The α transition structure **4b** occurs earlier, in a geometrical sense, than in the case of the lithiated system: comparing

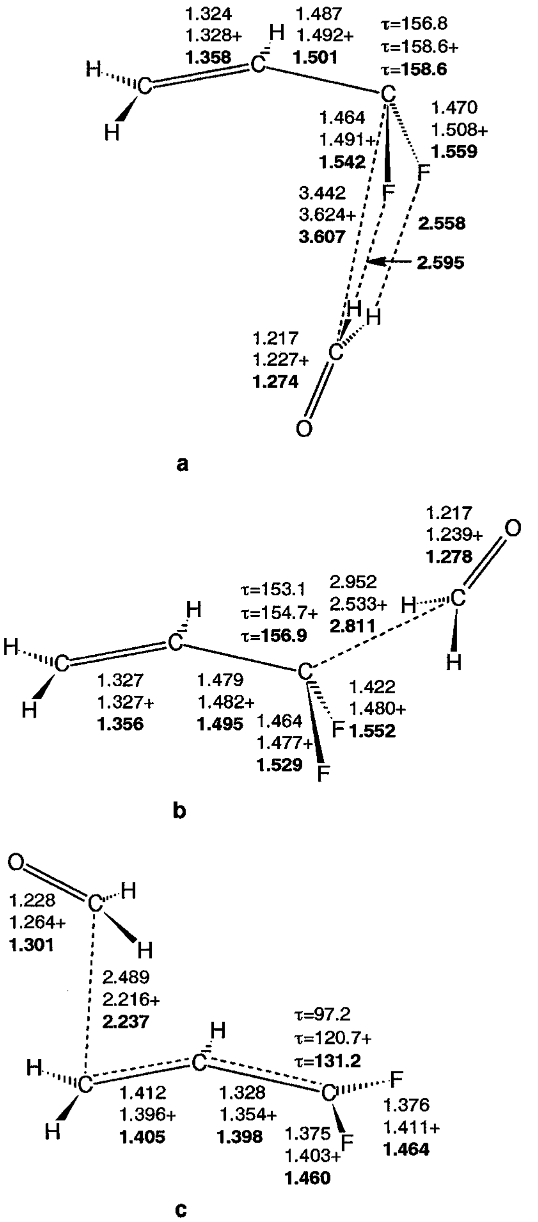


Figure 4. (a) The ion−dipole complex between formaldehyde and the 1,1-difluoroallyl anion; (b) the α-transition structure; (c) the γ-transition structure. Interatomic distances in angstroms, angles in degrees (plain figures: HF; marked with a +: with diffuse functions; bold: MP2).

for instance the HF/3-21G(*) values, we observe that the C−C$_\alpha$ distance is 0.20 Å larger than in **2b**. In the case of the γ transition structure **4c**, the C−C$_\gamma$ distance is larger by 0.25 Å with respect to the value found in **2c** and would suggest an earlier occurrence with respect to it; however, the C$_\alpha$−C$_\beta$ and C$_\beta$−C$_\gamma$ bond lengths are 0.07 Å shorter and 0.05 Å larger than those optimized in **2c**, respectively. In the γ transition structure the τ angle shows large variations with respect to its value in the σ complex, as observed in the previous cases. Its value in **4c** exhibits a significant dependence on the computational level.

The computed α and γ barriers for both dichloro and difluoro free anions appear to be consistent with the reaction energies: the α product is in fact always computed to be much more stable than the γ (seeTable 2; geometries not shown). Indeed, in all cases examined so far, the exothermicity of the γ attack has been always found to be lower than the α: however, while the γ exothermicity in both lithiated systems is significantly enhanced with respect to the free anions, the α is almost unchanged. Thus, the exothermicity factor can contribute to discriminate between the two pathways more in the anions than in the lithiated systems.

Addition Reaction of Formaldehyde to (1,1-Dichloroallyl)potassium. Experimentally, the dichloroallyl system reacts preferentially with the α terminus in the presence of a potassium counterion.[13a] This model system was studied with the purpose of comparing the geometrical features of the critical points with those of the related structures in the lithiated systems and free anions, as well as the reaction energetics. However, it must be kept in mind that the real situation in the experimental conditions (when using a Schlosser superbase,[13a] i.e. in the presence of a mixture of alkyllithium and potassium alkoxide) could be more complex than that considered here by the simple model "(*gem*-dichloroallyl)potassium".[13b] The geometry of the σ-complex (Figure 5a), is similar to **1a**, apart from the expected long bonds around the potassium cation. The electrostatic interaction with the two moieties which it holds together must be smaller than in the lithium case, and some values of the geometrical parameters involving C$_\alpha$ appear to be intermediate between those of **1a** and **3a**.

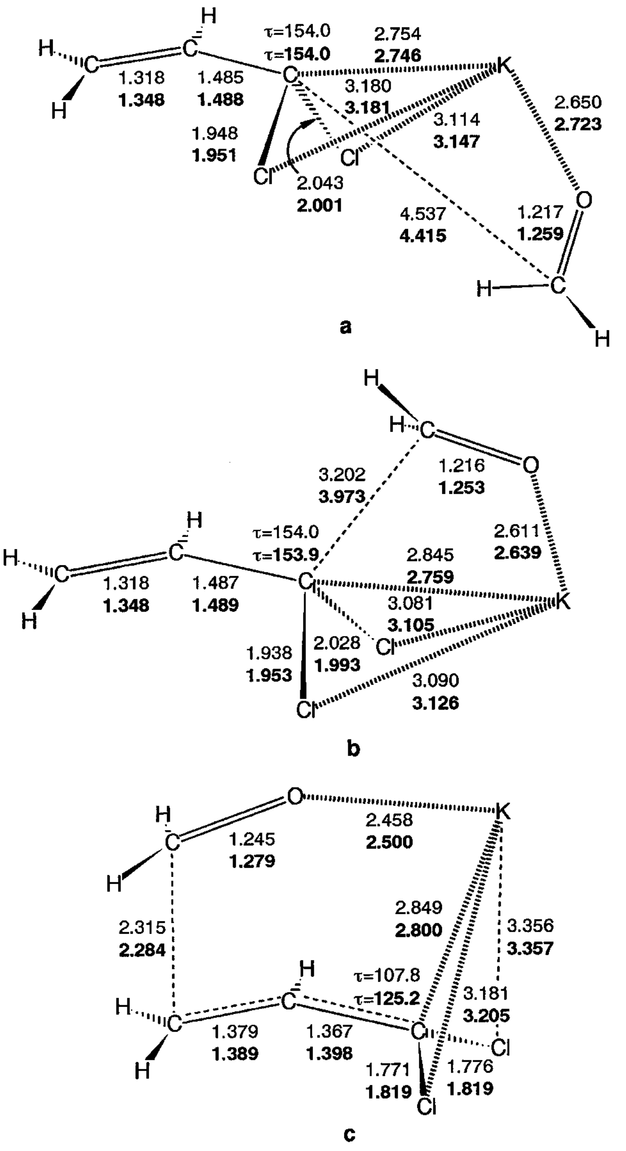


Figure 5. (a) The σ-complex between formaldehyde and (1,1-dichloroallyl)potassium; (b) the α-transition structure; (c) the γ-transition structure. Interatomic distances in angstroms, angles in degrees (plain figures: HF; bold: MP2).

The relative height of the computed energy barriers on the α and γ pathways is similar to that computed for the free dichloro anion (Table 2), but very different from that found for the lithiated dichloro system (Table 1): the MP2 γ barrier is indeed about twice the α. The geometrical parameters of the α transition structure (Figure 5b) do not show large variations of the bond lengths around K$^+$; the CO bond is not stretched with respect to its length in the σ-complex, while the C−C$_\alpha$ distance is still very large. These features indicate that the α transition structure occurs very early on the reaction path (comparison with **1b** shows that the α transition structure is earlier when K$^+$ is involved and later when the counterion is Li$^+$). The geometrical parameters of the γ transition structure **5c**, on the other hand, show a significantly shorter O−K$^+$ bond length, accompanied by a rather short C−C$_\gamma$ distance. The allylic moiety has undergone at the same time a considerable structural change: the C$_\alpha$C$_\beta$ and C$_\beta$C$_\gamma$ bonds have in **5c** almost equal lengths, and the CCl$_2$ group is close to planarity. These

---

(13) (a) See for instance: Schlosser, M. *Mod. Synth. Methods* **1992**, 6, 227. Mordini, A. In *Advances in Carbanion Chemistry*; Snieckus, V., Ed., JAI Press Inc.: Greenwich, CT, 1992; Vol.1, p 1. (b) The theoretical study of the reactivity modes of Schlosser's LICKOR superbase, carried out by considering the intervention of different aggregates and their structural and electronic features, suggests that one effective form of the reactant behaves as a *loose* potassium alkide molecule, with a K$^+$−C$^-$ distance of ca. 3.02 Å, instead of the more usual 2.88−2.89 Å. Ghigo, G.; Tonachini, G.; Venturello, P. *Tetrahedron* **1996**, *52*, 7053−7062.

(14) (a) These formulae, as implemented in the GAUSSIAN system (ref 10), are based on the perfect gas, harmonic oscillator, and rigid rotor approximations. Given that low frequency contributions are present, it must be admitted that the approximation used is inaccurate. In the cases studied, however, only one low-frequency mode could be properly assimilated to a rotation, and the resulting correction to the standard treatment would be insignificant. (b) For (1,1-dichloroallyl)lithium the difference is reduced by ca. 2.0 kcal mol^{-1} (from 4.2 to only 2.0 kcal mol^{-1} at the MP2 level; for (1,1-difluoroallyl)lithium the already large difference between the two barriers is raised by 1 kcal mol^{-1}. As illustration, the MP2/3-21+G(*) results are shown below (kcal mol^{-1}, relative to the complexes; T = 183 K):

Structure			$\Delta H^‡$	$-T\Delta S^‡$	$\Delta G^‡$
Cl-Li	α T.S.	**1b**	8.5	0.2	8.6
	γ T.S.	**1c**	5.1	1.5	6.6
F-Li	α T.S.	**2b**	3.6	1.0	4.5
	γ T.S.	**2c**	15.5	1.0	16.5
F anion	α T.S.	**4b**	0.4	0.8	1.2
	γ T.S.	**4c**	7.6	1.6	9.2

parameters can be compared with those reported for the γ transition structures of the lithiated system, **1c**, and free anion, **3c**: the latter appears to be moderately later than both **1c** and **5c**, approximately to the same extent. The exothermicity of the two processes seems to be consistent with the computed barriers, in that the more exothermic process shows the smaller barrier. With the dichloro free anion as a reference, it can be observed that the potassium cation stabilizes more the reactant than the products, thus reducing both α and γ exothermicities by 10 and 7 kcal mol^{-1}, respectively.

Estimate of the Reaction Free Energies. The free energies for the two attacks were computed for all systems at the HF and MP2 levels, by use of the standard formulae.[14a] The main information is that in all cases the ordering of the two barriers is not altered by the approximate corrections so introduced.[14b] However, the $-\Delta S^{\ddagger}$ term is larger for the γ pathway, thus favoring the α pathway. This can be attributed to the formation of a γ cyclic transition structure involving all carbon atoms, as well as the lithium counterion and the carbonyl oxygen.

Summary of the Observed Trends. Some prominent features shown by the five systems just examined are summarized and compared in this subsection for sake of convenience (reference will be made to MP2 energy differences).

(1) Regioselectivity. The dichloro free anion, (dichloroallyl)potassium, and (difluoroallyl)lithium are all decidedly more reactive at the α terminus, while the reaction involving (dichloroallyl)lithium is the only one which exhibits some preference for the γ attack (this could suggest that the inclination toward the γ pathway must originate, at least indirectly, from the very interaction of lithium with the chlorine atoms).

(2) Role of the Cation in Affecting the Exothermicity. The α attack is more exothermic than the γ for all systems (abscissa values in Figure 6). In the case of the free anions, rather large exothermicity differences are found, in favor of the α product: 15 and 20 kcal mol^{-1} for the dichloro and difluoro anions, respectively. In both dichloro and difluoro systems, a lithium cation stabilizes the anionic reactant and the α product to the same extent, leaving the α exothermicity found in the anion reactions unchanged. In contrast, Li^{+} stabilizes both dichloro and difluoro γ products to a larger extent: by 11 to 13 kcal mol^{-1}, respectively, relative to the anions (the γ product appears to be less stable than the α because of its structure, presenting a double carbon−carbon bond with geminal dihalo substitution, but, in the lithiated systems it apparently recovers some stability). In contrast, it has just been observed that the potassium cation stabilizes more the reactant than the products (dichloro anion as a reference) thus reducing both α and γ exothermicities by 10 and 7 kcal mol^{-1}. The smallest "$\gamma - \alpha$" difference in reaction energies (4 kcal mol^{-1}) is thus found for (dichloroallyl)lithium; this difference is comparable to that shown by the (difluoroallyl)lithium system (6 kcal mol^{-1}). For (dichloroallyl)potassium a larger difference is found, almost 12 kcal mol^{-1} (rather close to that observed in the dichloro anionic system).

(3) Reaction Energy Barriers vs Exothermicity. All systems, but (dichloroallyl)lithium, show a clear proportionality between "$\gamma - \alpha$" differences in reaction barriers and the relevant "$\gamma - \alpha$" differences in reaction energies, i.e. the more exothermic the reaction, the lower the barrier (negative slopes in Figure 6). (Dichloroallyl)lithium has anti-Hammond behavior: therefore, exothermicity does not seem to be a dominant factor in giving rise to a preference for one of the two termini. It can also be evinced from Figure 6 that the cations stabilize the reactants more than the corresponding transition structures, that potassium raises the barriers while decreasing the exothermicity (line shifted to the left) and that lithium raises the barriers and increases the γ exothermicity (γ-points shifted to the right).

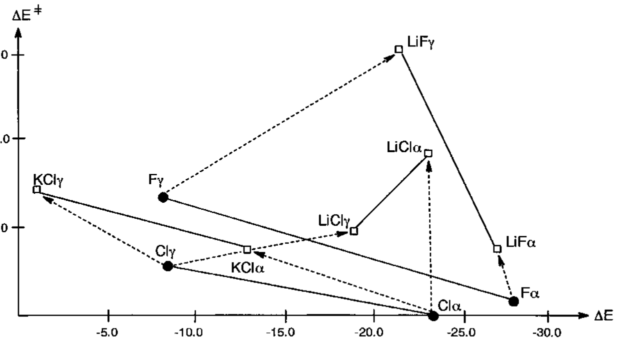
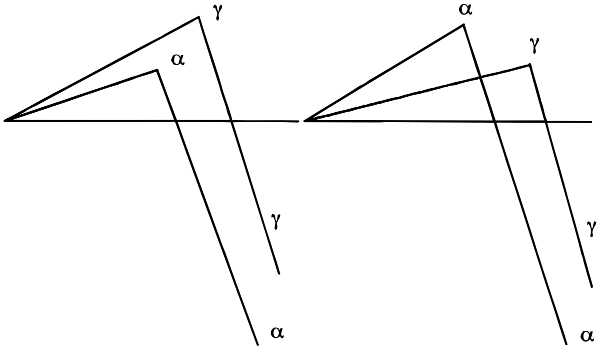


Figure 6. Activation energies vs reaction energies (MP2 data) for the anionic (black circles) and metalated (white squares) systems. Solid lines relate the values relevant to the same system, while dashed arrows emphasize the changes found in going from the reference anionic systems to their metalated counterparts.

Scheme 3



(4) Relative Earliness of α and γ Transition Structures. All γ transition structures are less stable and "later", in a geometrical sense, than the corresponding α, consistently with the Hammond postulate. (Dichloroallyl)lithium is again an exception.

Qualitative Interpretation of the Observed Trends. The destabilization of the reactants, which grows up in the first part of the reaction pathway, and the exothermicity factor, both obviously concur to an earlier or later occurrence of a transition structure, as well as to the barrier height. To discuss how the interplay of these factors can give rise to a different regioselectivity, the qualitative sketch presented in Scheme 3 may be of some help. The points defining a reactant position on the "reaction coordinate" axis are arbitrarily brought to coincide, on the left, for both α and γ attacks. The destabilization of the system develops more and more as the reaction proceeds toward the transition structure, and the resulting slopes depend on the system considered.[15a] Differences in exothermicity, on the other hand, are reflected in the descending lines on the right, which have been drawn approximately parallel for simplicity. The computational data are qualitatively consistent in all cases with the leftmost plot, except for the (dichloroallyl)lithium case, in which they would fit the

Table 3. Contributions to the Destabilization Undergone by the Reactants[a]

		anions			Li systems			K system		
		ΔE(A)	ΔE(B)	R	ΔE(A)	ΔE(B)	R	ΔE(A)	ΔE(B)	R
α pathway:	F	0	0	2.81	1	4	2.72	–	–	
	Cl	0	0	–	1	14	2.92	0	0	3.97
γ pathway:	F	10	4	2.24	14	0	2.41	–	–	
	Cl	5	3	2.34	7	1	2.46	14	0	2.28

[a] kcal mol^{-1}. See text for the definitions of ΔE(A), ΔE(B), and R.

situation sketched in the plot on the right. Thus, Scheme 3a shows that even if the destabilization were the same for the two pathways, the relative energy and earliness of the two transition structures would not change and would be entirely dictated by the exothermicity factor. In contrast, Scheme 3b is pertinent to a system undergoing a smaller destabilization in correspondence with the γ attack: a difference in stability between the α and γ products similar to that of Scheme 3a yields again an earlier α crossing point, but this is associated to a higher barrier. In summary, exothermicity stipulates the relative earliness of the transition structures in *all* cases, but not the relative height of the barriers: for (dichloroallyl)lithium, the importance of destabilizing factors is crucial.

An estimate of the destabilization undergone by the different reacting systems would be helpful, because it could be combined with the computed exothermicities, within the frame offered by Scheme 3. It can be first considered that, on going from the electrostatic σ-complexes to the α or γ transition structures, the overall change in nuclear configuration can be conceptually dissected into the following main components: (A) the dihaloallyl(metal cation) skeleton is deformed from its optimum σ-complex geometry; (B) the relative positions of the metal cation (M) and carbonyl group are altered, mainly because of a change in the value of the MOC angle, and the carbonyl too is slightly deformed; (C) the aldehydic and dihaloallylic moieties come closer one to the other by pivoting around the alkali metal cation. The combination of the three geometrical changes brings about the observed destabilization of the reacting system:[15b] indeed, the destabilizing contributions can be thought of as being present to the smallest extent in the σ-complex and to the largest extent in the transition structure. We shall consider factors A and B as superimposed to the unknown energetic effect relevant to factor C. The importance of factor C, which depends on the distance between the two reacting molecules, will be greater for later transition structures (the C(aldehyde)$-$C$_\alpha$ or $-$C$_\gamma$ distance, R, can be taken as an approximate measure of this distance). Thus, in correspondence to the transition structure geometries, factor C will be in all cases more important for the γ pathway, because all γ transition structures are later ($R = 2.28$ to 2.46) than the corresponding α ($R = 2.72$ to 3.97). Factor C will as a consequence favor the α pathway with respect to γ; among γ transition structures, the longest R is presented by (dichloroallyl)lithium. The estimate of the relative importance of the contributions to the energy barriers arising from the structural changes A and B can then be attempted by way of two series of MP2/3-21G(*) computations (with added diffuse functions for the anions), in which the energy of one part only of the reacting system is computed; the geometry of this subsystem is that optimized in the σ-complexes and α or γ transition structures. Thus, the results of the calculations carried out on the dihaloallyl(metal cation) subsystems alone will be labeled ΔE(A), while those carried out, in a parallel way, on the formaldehyde(metal cation) subsystem will be labeled ΔE(B). The estimates of the destabilization contributions, whose aim is to provide qualitative trends, are given in Table 3 as integer figures (for sake of convenience, also R values are reported).

Free Anions. The estimate of the two destabilizing contributions for the free anions works in the same sense as the exothermicity factor (the less destabilized pathway is also the more exothermic), and their combination yields a picture going even beyond that sketched in Scheme 3a. In the case of the α pathway, for the difluoro anion, both ΔE(A) and ΔE(B) contributions are tiny, and their sum is estimated to be very close to zero; the same is true also for the dichloro anion, because the presence of the shoulder zone sets any estimate to zero. Moreover, if the computed energy barriers are considered (Table 2), factor C seems to be almost absent. These results contrast those for the γ pathway: in this case, ΔE(A) values are larger than ΔE(B) for both anions, and their sum is larger for the difluoro anion than for the dichloro. These results can be combined with the computed exothermicity difference (see Table 2), which amounts to 15 kcal mol^{-1} in favor of the α pathway. Thus, if the sum of these two contributions is the main discriminating factor in the ascending part of the two pathways, it generates a situation similar to that depicted in Scheme 3a (later and higher-energy γ transition structure). Of the two systems, the difluoro presents the higher γ barrier (compare ΔE(A), ΔE(B), and R from Table 3 with the energy barriers reported in Table 2).

Metalated Systems. In the case of the α pathway, the ΔE(A) terms are found to be very small for both difluoro and dichloro lithiated systems; this is true also for the potassium dichloro system. Rather modest deformations of the metal$-$dihaloallyl skeleton are indeed involved in the α transition structures. In the potassium dichloro case, also the ΔE(B) term is very small. In contrast, this term is sizable in the case of lithium dichloroallyl, in which the COLi angle value has *dropped* by 23°. The destabilization is more than three times that estimated for F, in which case the COLi angle variation is only $-4°$.[16a,c] The substantial decrease of this angle for the dichloro system can be put in relation to the Cl$-$

---

(15) (a) The energetic effect related to the formation and disrupture of all bonds directly involved in the reaction are destabilizing in the first part of the reaction path, and stabilizing in the second one, beyond the transition structure. The energy rise is related to the destabilization of the spin-coupling pattern typical of the bonding situation of the reactants, as well as to electrostatic, steric, and deformation factors. Similarly, the exothermicity factor is related to the effectiveness of the stabilizing new (productlike) spin-coupling pattern as well as to steric, deformation, and electrostatic factors. All these factors depend on the geometry variations undergone by the reacting system. (b) Because in computations A and B the two subsystems maintain the electronic structure (bonding) of the reactants, the information recovered with these calculations is pertinent to all of the above-mentioned factors (the same factors contribute to factor C, i.e. to the destabilization due to the very approach of the aldehydic and allylic molecules).

Li interactions (compare for instance the structural differences present in both initial complexes and α transition structures in Figures 1 and 2). Thus, *the deformation of the aldehyde−metal cation part of the system gives rise to the dominant term for the α pathway and is especially important for the lithium dichloro system*. The computed α barrier for this system is twice as high as that for the other two metalated anions (Table 1). For the potassium dichloro system, the lower exothermicity probably equilibrates the vanishing destabilization brought about by factors A and B, thus producing a barrier which is comparable to that of the lithium difluoro system.

In the case of the γ pathway larger deformations are involved for all metalated systems. However, the ΔE(A) term for both lithium difluoro and potassium dichloro systems is just twice that computed for the lithium dichloro. The lesser destabilization of the lithium dichloroallyl system could be directly related to the Li−Cl interactions. In contrast with the results relevant to the α pathway, the ΔE(B) terms are quite small for all metalated systems.[16b,c] In summary, *for the γ pathway, the destabilizing effect is dominated by the dihaloallyl−metal contribution for all metalated systems; the smallest estimate is for the lithium dichloro system*. Factor C, which is not estimated, could give a non negligible contribution for the γ attack, because the distances between the two reactants are shorter than for the α attack (Table 3); among the γ transition structures, the lithium dichloroallyl−formaldehyde system presents the largest *R*, and structure **1c** should consequently suffer a smaller destabilization.

The results for the two different pathways suggest that the height of the α barrier is associated to the presence of the counterion and to its interactions with the atoms belonging to the α terminus, while the γ barrier (already present in the free anions) appears to be more strictly related to the structural changes of the allylic skeleton. The above estimates, combined with the exothermicity data, can offer an interpretation of the energy barriers conforming to the situations sketched in Scheme 3.

Conclusions

The overall picture obtained in this study compares well with the available experimental results. The model based on an ionic mechanism seems to be adequate and provides a basis for an attempt to qualitatively rationalize the very different regioselective behavior shown by (dichloroallyl)lithium with respect to the other *gem*-dihalo-substituted allylic systems. The comparison of the results obtained for the free anions and the metalated systems obviously suggests that the origin of the α barrier (close to zero in the free anions) is associated to the presence of the counterion; in contrast, the γ barrier (although lower for the free anions than for their metalated counterparts) appears to be more strictly related to the structural changes of the allylic skeleton. The barrier heights and earliness of the relevant transition structures are related to the interplay of an exothermicity factor and destabilizing interactions which act in the first part of the reaction pathways. The exothermicity of the γ attack is always found to be lower than the α: however, while the γ exothermicity in both lithiated systems is significantly enhanced with respect to the free anions, the α is almost unchanged. Thus, the exothermicity factor can contribute to discriminate between the two pathways more in the anions than in the lithiated systems. In all cases exothermicity stipulates the relative earliness of the transition structures (α is the more exothermic pathway, and consequently the α transition structure is the earlier). However, for (dichloroallyl)lithium, exothermicity does not seem to be a dominant factor in giving rise to a preference for one of the two termini: the importance of destabilizing factors is crucial in determining the regioselective behavior. Moreover, the results indicate that for (dichloroallyl)lithium the inclination toward the γ pathway must originate, at least indirectly, from the very interaction of lithium with the chlorine atoms.

Acknowledgment. Financial support from the Italian M.U.R.S.T. and from the Italian C.N.R. (within the “Progetto Strategico Tecnologie Chimiche Innovative”) is gratefully acknowledged. The IBM RISC-6000/550 was assigned to this laboratory by C.N.R. within the project “Calcolo Avanzato in Chimica”.

Appendix

Calibration of the Computational Level. The MP2 calculations presented and discussed in this paper were carried out in conjunction with two rather modest basis sets: 3-21G(*), used for the metalated dihaloallyl systems, and 3-21+G(*), used for the free anions. These basis sets have d functions only on the chlorine atoms, and the former is without diffuse functions. The tests carried out in order to assess the degree of reliability of this computational level consists of two sets of MP2/6-31G(d) and 6-31+G(d) optimizations of the structures **2a**, **2b**, and **2c** of the neutral lithium difluoroallyl system. The 6-31G(d) basis set is larger and polarized in a more balanced way than 3-21G(*); in the second series of calculations diffuse sp functions are added to this basis. Unfortunately, this kind of calculation was unaffordable for the lithium and potassium dichloro systems and can thus be intended only as a calibration of the MP2/3-21G(*) computational level used throughout.

The energy differences obtained by fully optimizing the structures at the MP2/6-31G(d) level[17] for the lithium difluoro case are 2.1 (α barrier) and 5.7 kcal mol^{-1} (γ barrier). Three points can be considered. (i) The two barriers can be compared with those in Table 1. Both MP2/3-21G(*) barriers are higher than the MP2/6-31G(d) ones. Although this comparison is not completely satisfactory, because the γ barrier results are more overestimated than the α, nevertheless they are still in the same order. In this respect, the results obtained seem to be in sufficient agreement with those collected at the lower computational level. (ii) Making reference to the MP2/6-31G(d) single point energy computations reported above, which provided barrier values of 1.5 and 6.1 kcal

---

(16) (a) α Pathway: in the potassium dichloro case, the COK angle value increases from 121.5° to 136.5°; for lithium difluoroallyl, the COLi angle decreases from 125.4° to 102.7°; in the analogous difluoro system it changes from 115.1° to 110.5°. (b) γ Pathway: the COM angle value is increased by: 17° (lithium difluoro, from 115.1° to 132.3°), 12° (lithium dichloro, from 125.4° to 137.8°), and 33° (potassium dichloro, from 121.5° to 154.7°), in going from the σ-complexes to the γ transition structure. (c) A simple test carried out at the same computational level on the formaldehyde−lithium cation complex (by optimizing for several values of the LiOC angle the remaining geometrical parameters) confirms that a *decrease* of the COLi angle from its optimum value (ca. 120°) in the complexes is energetically more important, while an increase is not as important (the energy surface becomes rather flat).

mol^{-1}, a good agreement is observed: it can thus be stated with some confidence that the single-point results are informative (only these are available for the lithium dichloro system). (iii) The two barriers are calculated to be 2.1 and 4.9 kcal mol^{-1}, respectively, by MP2/6-31+G(d) optimizations:[17] this last result shows that diffuse functions are not crucial to assess the reaction energetics of the neutral systems and validates the use of a basis set without diffuse functions for the three metalated systems.

The optimum geometries obtained in these tests (only the main parameters are reported in Table 4) allow us to examine the structural consequences of the use of the smaller basis set in the MP2 optimizations. For instance, comparing Table 4 with Figure 2 (bold figures), we observe the following main differences: shorter C_α−F and C_α−Li distances at the 6-31G(d) level, accompanied by some elongation of the O−Li and Li−F distances. Adding diffuse functions brings about a further shortening of the C_α−F bonds (but only in the complex) and C_α−Li (mainly in the complex); O−Li distances become smaller, and Li−F distances larger (the latter only in the complex). In summary, the sufficiently good agreement between the different sets of barrier values is a consequence of the limited differences found in the optimum geometries. This is particularly true for the comparison of the 6-31G(d) and 6-31+G(d) sets of data.

Table 4. Main Geometrical Parameters Optimized in the Test Calculations[a]

	complex **2a**		α T. S. **2b**		γ T. S. **2c**	
	A	*B*	*A*	*B*	*A*	*B*
C_α−C_β	1.472	1.465	1.472	1.470	1.422	1.418
C_β−C_γ	1.341	1.344	1.341	1.345	1.372	1.374
F−Li	1.516	1.499	1.525	1.528	1.472	1.474
F′−Li	1.544	1.514	1.533	1.537	1.372	1.382
Li−C	2.278	1.930	2.308	2.297	2.069	2.063
Li−O	1.962	1.895	1.947	1.892	1.854	1.798
R	3.276	3.752	2.984	2.977	2.299	2.343

[a] Column A: MP2/6-31G(d); column B: MP2/6-31+G(d). Of the two fluorine atoms, F is the closest to the reader in Figure 2, F′ the farthest.

JO951620Z

---

(17) The total energies from MP2/6-31G(d) optimizations are the following: (**2a**) −436.588900, (**2b**) −436.585567, (**2c**) −436.579850. Those from MP2/6-31+G(d) optimizations are the following: (**2a**) −436.627188, (**2b**) −436.623828, (**2c**) −436.619372.