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REGIOSELECTIVITY IN LITHIUM, SODIUM AND POTASSIUM CHLOROALLYL SYSTEMS. AN *AB INITIO*-THEORETICAL AND EXPERIMENTAL STUDY

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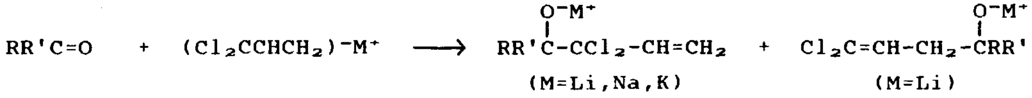
Abstract

The computed structural and electronic features of the title compounds describe the sodium and potassium systems as more inclined to CCl_2 regioselectivity with carbonyl electrophiles than the analogous lithium compounds. Some experimental results confirm this expectation.

Introduction

In the last years *gem*-dichloroallyl-lithium has been synthesized and its reactivity studied experimentally by Seyferth, Mauze' and coworkers.[1,2] This system has been shown to behave as an ambident nucleophile when reacting with carbonyl compounds, yielding different products of attack depending on the substituents on the carbonylic carbon atom. Indeed, it presents a whole spectrum of product distributions going from a complete CCl_2 attack to a complete CH_2 attack.[2] On the other hand the reactivity of *gem*-dichloroallyl-potassium has been recently studied experimentally in this laboratory,[3] providing the interesting result of an almost complete CCl_2-selectivity toward carbonyl compounds (Scheme 1).



$$RR'C{=}O \quad + \quad (Cl_2CCHCH_2)^-M^+ \longrightarrow \underset{(M=Li,Na,K)}{RR'\overset{O^-M^+}{\overset{|}{C}}-CCl_2-CH{=}CH_2} \quad + \quad \underset{(M=Li)}{Cl_2C{=}CH-CH_2-\overset{O^-M^+}{\overset{|}{C}}RR'}$$

Scheme 1

The rationalization of these results is complicated by the existence of factors that can in principle affect the structural and electronic properties and the behaviour of these systems, such as: (i) the unknown degree of aggregation (allyl-lithium itself has been shown by Winchester, Bauer and Schleyer to exist in the usual conditions as an asymmetric dimer, while allyl-sodium and allyl-potassium have been argued to be present as symmetric, presumably monomeric, structures);[4] aggregation itself is a function of temperature, increasing with increasing temperature; (ii) the degree of interaction of the counter-ion with the substituted allylic system in the monomer: it ranges in principle from an almost free anion, a solvent separated ion pair, to a true bonding situation where the cation and the anion would interact much more significantly.[5]

In the present theoretical study an extreme situation of deaggregation has been assumed (the monomer-dimer equilibrium is under investigation and will be the subject of a separate communication).[6] Moreover, the different degrees of interaction of the cation with the substituted allylic anion are taken into account by modelling just two extreme situations, i.e. "no interaction" and "tight interaction". The systems are thus studied by determining the stable structures of two substituted allyl anions, 1-chloropropenide and 1,1-dichloropropenide, and comparing them with those originating from the tight association of the anions with a lithium, sodium or potassium cation (how this picture can be modified by considering the interaction of the metallated species with some oxygenated solvent molecules, as a first approximation for a first solvation shell, is also under study).[6] The present investigation aims to attempt a first interpretation (within the approximations discussed above) of the markedly different regioselectivity shown by these systems in function of the counter-ion, on the basis of the structural and electronic features of the lithium, sodium and potassium dichloroallyl monomers. Their electron distribution can be discussed in connection with the possibility of attack by a *hard* electrophile, while HOMO polarization can be examined as a factor which could determine the orientation of attack of a *soft* electrophile. In connection with this purpose, the results of some reactions of *gem*-dichloroallyl-lithium, -sodium and -potassium with substituted benzaldehydes are also reported. A comparison can also be drawn between mono and dichloroallyl-lithium and the analogous fluoro-substituted systems, that have been studied theoretically in a previous paper[7] at the same computational level (the *gem*-difluoroallyl-lithium system shows a different regioselective behaviour than the dichloro).[8]

Theoretical method

The energy minima corresponding to stable structures have been determined by complete and unconstrained optimization of the geometrical parameters by gradient methods.[9] These computations were carried out at the RHF level of theory, using the split-valence shell 3-21G basis set,[10a] augmented with diffuse *sp* functions[10b] on carbon and chlorine atoms and with polarization *d* functions on chlorine. This basis set, containing neither diffuse nor *d* functions on the cations, will be labeled 3-21+G[*] throughout this paper. The computations have been performed using the GAUSSIAN82 and 88 series of programs[11] on an 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

Structural features of the free anions. In a previous study,[7] carried out at this same computational level, the unsubstituted allyl anion was found to be stable only in correspondence of a completely planar structure. The optimized structures of the mono and dichloro allyl anions show that the Cα carbon is pyramidalized only in the *gem*-disubstituted anion (Figure 1; RHF/3-21+G[*] bond lengths in Ångstrom, angles in degrees; dihedral angles relevant to atom X are defined as angles between the XCC and CCC planes and reported in square brackets).

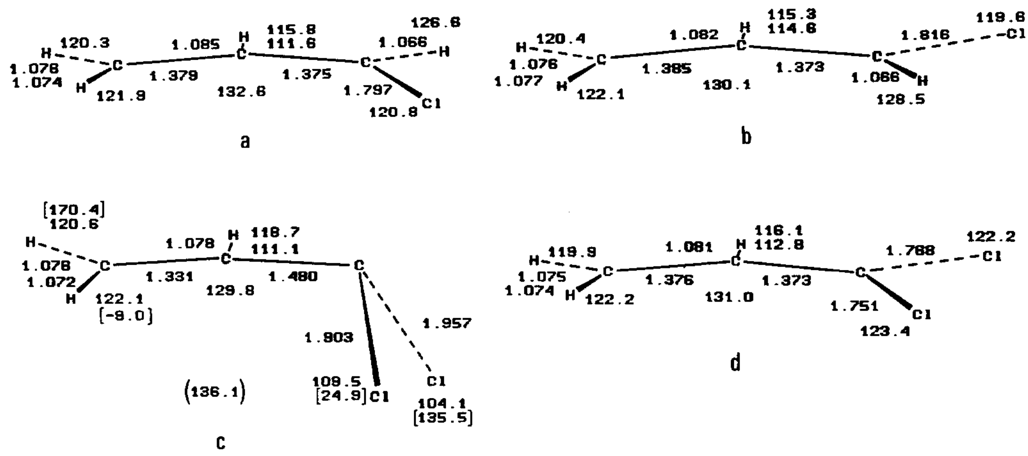


Figure 1

The degree of pyramidalization in the dichloro anion is reported in Fig. 1c (τ angle, in round brackets).[12] The main difference between the description of the electronic structure of the dichloro species and that of the allyl anion is thus the desappearance of the allylic fully delocalized π system with disubstitution of a terminal carbon atom. The pyramidalization of the CCl_2 group leads to a rather localized system, as shown by the Cα-Cβ (1.480 Å) and Cβ-Cγ (1.331 Å) bond lengths, that approximate the tipical values for single and double CC bonds.[13] Two equivalent 1,1-dichloropropenide pyramidalized structures, obtained by reflection through the CCC plane, are connected by a planar structure, whose optimized geometry bears some resemblance to the unsubstituted allyl anion (Fig. 1d). The analytical Hessian computation shows that this critical point is another minimum, showing no imaginary frequencies. The Hessian eigenvector related to the lowest eigenvalue (0.004) is dominated by the inversion motion of the CCl_2 group. This structure is less stable than the pyramidal (Table 1).

In the case of 1-chloropropenide, the two possible non-equivalent structures, with the CCl bond syn and anti with respect to the Cβ-Cγ bond, are found to be planar (Fig. 1a,b). Being not pyramidalized at the α carbon center, the structures of 1-chloropropenide depart less from that of the allyl anion. For instance, considering the syn conformation, the Cα-Cβ bond length is 1.375 Å and the Cβ-Cγ bond length 1.379 Å. These values are rather close to the CC bond length value in the allyl anion, 1.387 Å. Similar structural features were found for mono and difluoropropenide,[7] but in the case of double fluorine substitution the α carbon was more pyramidalized and some pyramidalization was present in 1-fluoropropenide too. The structural features just discussed determine both the electron distribution and the polarization of the molecular orbitals in the free anions. These effects will be examined below for both the free and metallated anions.

TABLE 1

Free Anions. Total and relative energies.[a] HOMO polarization.[b]

		E	ΔE	P(Cα)/ P(Cγ)
1-Chloropropenide				
syn planar	1a	-572.635579	0.00	1.295
anti planar	1b	-572.631840	2.35	1.156
1,1-Dichloropropenide				
pyramidal	1c	-1029.473230	0.00	3.906
planar	1d	-1029.466678	4.11	1.705

a: RHF/3-21+G[*] energies in Hartree, energy differences in kcal mol^{-1}.
b: the polarization of the HOMO is computed for Cα and Cγ as the sum of squares of the atomic orbital coefficients.

Structural features of the metallated species. Several stable structures have been found for both anions, in correspondence to different associations with an alkali metal counter-ion (Figures 2-4; RHF/3-21+G[*] bond lengths in Ångstrom, angles in degrees; dihedral angles relevant to an atom X are defined as angles between the XCC and CCC planes and reported in parentheses).

Lithium. The optimized geometries for the lithium 1-chloropropenide system are shown in Fig. 2a,b while those for the 1,1-dichloropropenide-lithium[14] system are shown in Fig. 2c,d. In the structures 2a and 2c lithium is bound to the α allylic carbon atom and to one or two chlorine atoms ("external" lithium). On the contrary, in the structures 2b and 2d both the Cα and Cγ atoms are substantially involved in bonding with the bridging counter-ion ("internal" lithium). The relative energies (Table 2) show that while in the monochloro system the "internal" (or bridged) structure is slightly more stable than the "external" one, the reverse is true for the dichloro system. The structures of the monochloro systems are in general closer to that of the unsubstituted allyl-lithium, while the dichloro are more pyramidalized (τ values) and show longer Cα-Cβ and shorter Cβ-Cγ bond lengths, respectively. These features (related to a more pronounced localization of the electron distribution to a "double bond zone" and a "lone pair zone") are more evident in the "external" structure than in the "internal" one, for both the monochloro and dichloro systems.

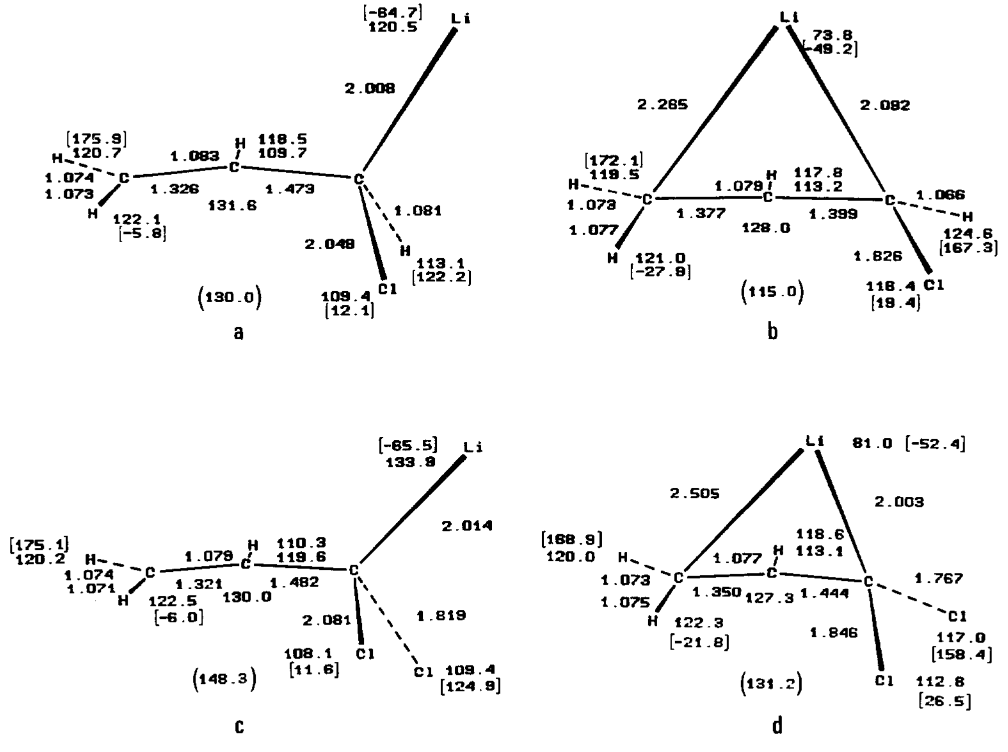


Figure 2

Sodium. In the case of sodium 1-chloropropenide any attempt to optimize a structure with the counter-ion in an "external" position yielded the geometry shown in Fig. 3a, where the Na-Cα bond is almost perpendicular to the plane of the allylic carbon atoms. Attempts to find a structure with sodium bridging between the α and γ carbons produced the same result. Thus sodium appears to be stable in a position that is intermediate between those defined for lithium as "external" and "internal"; although the situation is closer to the latter, the sodium atom cannot be considered as bridging between the two terminal allylic carbon atoms. In the case of sodium 1,1-dichloropropenide two stable structures were found: one with an "external" cation (Fig. 3b), and another with the cation in an "internal" position (Fig. 3c), similar to that of Fig. 3a.

TABLE 2

Metallated Systems. Total and relative energies.[a] HOMO polarization.[b]

		E	ΔE	P(Cα)/ P(Cγ)
Lithium 1-chloropropenide				
syn external	**2a**	-580.071623	1.00	1.527
syn internal	**2b**	-580.073224	0.00	1.493
Lithium 1,1-dichloropropenide				
external	**2c**	-1036.898437	0.00	1.626
internal	**2d**	-1036.892591	3.67	3.124
Sodium 1-chloropropenide				
syn	**3a**	-733.551911		1.303
Sodium 1,1-dichloropropenide				
external	**3b**	-1190.388039	0.00	8.363
internal	**3c**	-1190.377678	6.50	9.674
Potassium 1-chloropropenide				
syn	**4a**	-1168.745113		0.977
Potassium 1,1-dichloropropenide				
external	**4b**	-1625.502062	0.00	10.773
internal	**4c**	-1625.492972	5.70	9.552

a: RHF/3-21+G[*] energies in Hartree, energy differences in kcal mol^{-1}.

b: the polarization of the HOMO is computed for Cα and Cγ as the sum of squares of the atomic orbital coefficients.

The "external"-Na structure differs from the analogous "external"-Li structure (apart from the longer cation-Cα bond length) mainly in the cation-Cα-Cβ angle: ca. 134° for Li, ca. 161° for Na. The two stable structures differ by ca. 6.5 kcal mol^{-1} in favour of the "external" one. Both this energy difference and the large Na-Cγ distance even in the "internal" structure, would operate in favour of a CCl_2-regioselective attack by a carbonyl electrophile, if it is assumed that the counter-ion has to play an important role in stabilizing a four-center transition structure.[15]

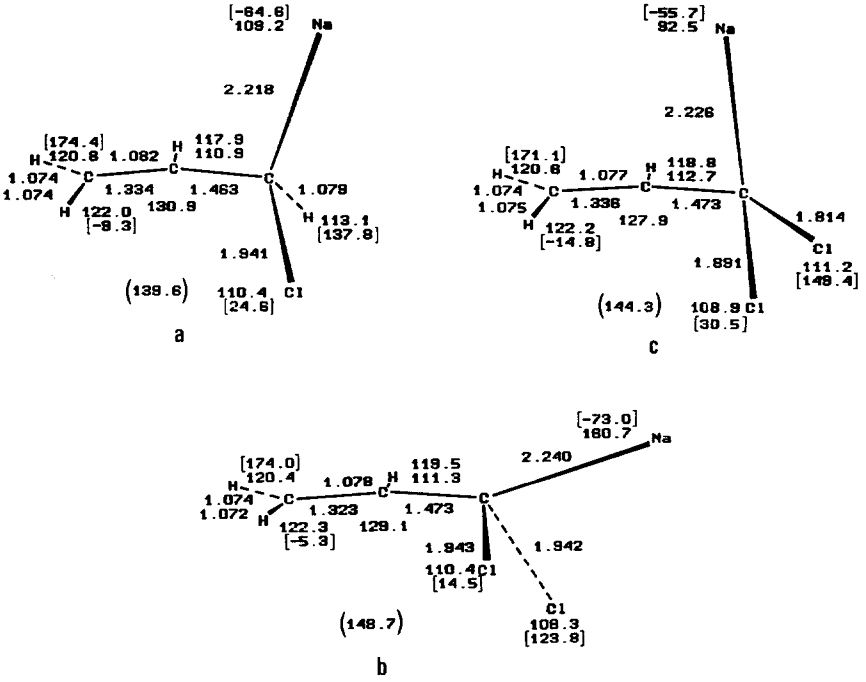


Figure 3

Potassium. As was the case with sodium, potassium 1-chloropropenide was found to be stable only in an "internal" position (Fig. 4a); the counter-ion cannot again be considered as bridging between the Cα and Cγ carbon atoms. In the case of potassium 1,1-dichloropropenide two stable structures were found: one with an "external" cation (Fig. 4b), and another with the cation in an "internal" position (Fig. 4c): these results for potassium closely parallel those obtained for sodium. The "external" and "internal"-K structures are similar (apart from the different cation-Cα bond lengths) to those optimized for sodium. The two stable structures differ by ca. 5.7 kcal mol^{-1} in favour of the "external" one. The same factors discussed above would operate also for this species in favour of an CCl_2-regioselective attack by a carbonyl electrophile.

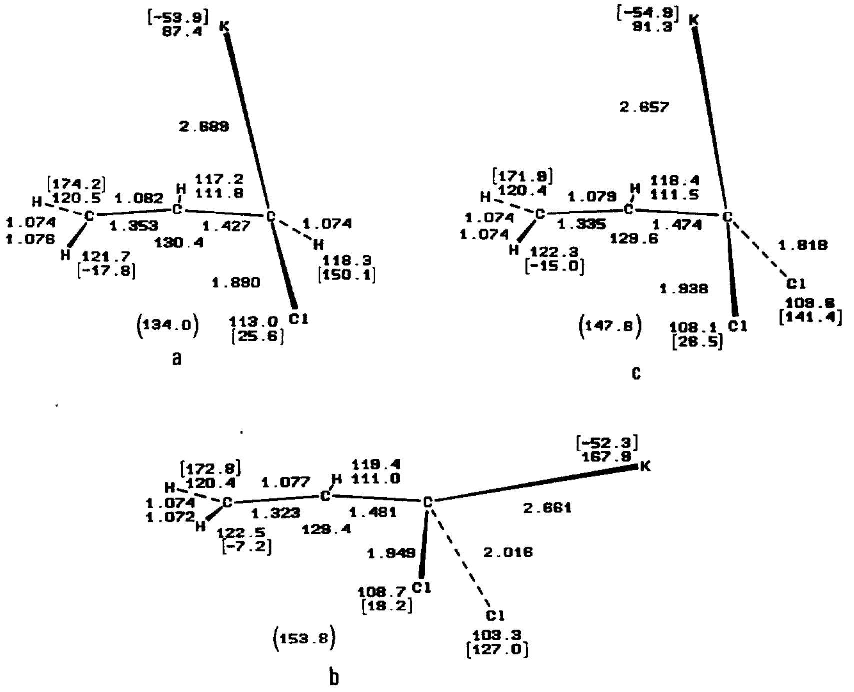


Figure 4

Electronic features of the free anions. The structural features determine both the electron distribution (to which *hard* electrophiles should be sensitive) and the polarization of the molecular orbitals, of which the highest occupied (HOMO) should be of particular importance in the case of attack by a *soft* electrophile. The effect of single and double chlorine terminal substitution on the electron distribution of the π allylic system can be examined in Figure 5, where the total electron density (on a plane 0.5 Å from the CCC plane and parallel to it) is plotted for the more stable structures of the mono and dichloro free anions (1a and 1c), and for the planar dichloro structure (1d). The π electron distribution appears to be consistent with the structural features discussed above. For the more stable planar structure of 1-chloro-propenide (1a), the description provided by the density plot is rather close to that of a delocalized π allylic system. A similar description is found for the less stable planar structure of both mono and dichloro anions (1b, 1d). On the contrary, in the case of the pyramidal structure of 1,1-dichloropropenide (1c) a Cα-Cγ "double bond zone" appears as clearly separated from a Cα "lone pair zone".

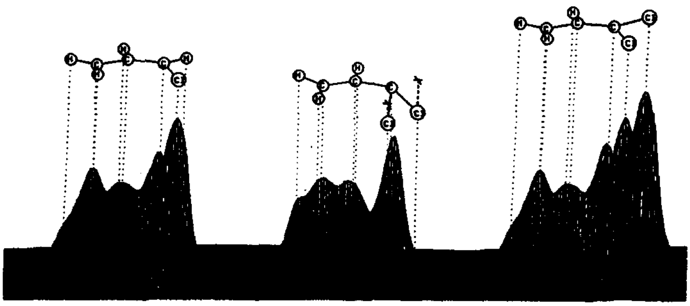


Figure 5

Electrostatic potential maps obtained at different distances from the CCC plane show that a *hard* electrophile, approaching the allylic system from "above", could sense an attractive electrostatic potential in correspondence of both the α and γ positions, with a preference for the former in the case of the disubstituted anion and for the latter in the case of the monosubstituted anion. Two of these maps, relevant to the more stable 1a and 1c structures and corresponding to a distance of 2.0 Å from the CCC plane, are shown in Figure 6.

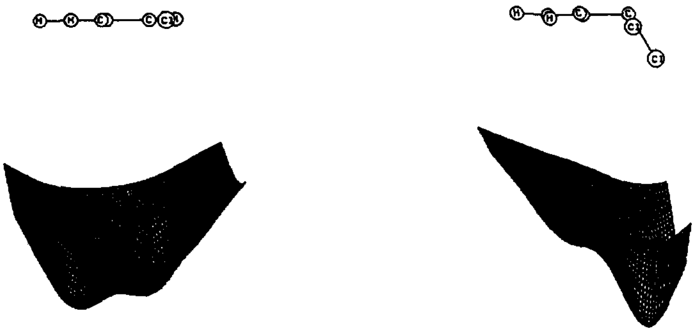


Figure 6

The HOMO polarization can be expressed in terms of a parameter, P(X), defined for each atom X in the molecule; its value is given by the sum of the squares of the HOMO atomic orbital coefficients belonging to that atom. The ratio between the Cα and Cγ P values is reported in the third column of Table 1 . It can be seen that the HOMO is always polarized toward the substituted carbon atom, more significantly in 1,1-dichloropropenide than 1-dichloropropenide.

These results show that, for the extreme case of the free dichloro anion (pyramidalized structure), both a *hard* electrophile, more sensitive to the charge distribution, and a *soft* electrophile, more sensitive to an "orbital interaction factor", would prefer to direct their attack toward the CCl_2 terminus of the molecule. On the contrary, the monochloro anion is expected to interact in a different way with *hard* and *soft* electrophiles (as indicated by the electrostatic potential maps and by the P ratios).

Electronic features of the metallated species. Although the overall systems have no net charge, still a clear polarization of the electron distribution is observable. This is shown again (Figure 7) by a series of electrostatic potential maps computed at three different distances R from the CCC plane. The dominant feature of these maps is the zone of strongly repulsive potential (for an approaching positive charge) generated by the counterion; this feature is present also at larger distances, where the attractive potential of the allylic part of the system is much less effective. For lithium any attractive contribution to the potential provided by the α carbon is overwhelmed by the cation repulsive field; the only attractive zone of the plots is in correspondence to the γ carbon.[16] On the contrary the sodium and potassium plots show two depressions in correspondence to the allylic skeleton, and the one originating from the α carbon becomes deeper at closer distances. It is fairly obvious that these different features originate at least in part from the geometries of the metallated species, namely from the relative positions of the α carbon and the counterion.

The HOMO polarization is reported again as P ratios for $C\alpha$ and $C\gamma$ in Table 2 (third column). It generally favours the substituted terminus (with the exception of 4a); this feature appears to be more pronounced when the anion is associated to Na or K. In the case of attack by a *soft* electrophile on an anionic system (where the allylic HOMO is rather high in energy) the more important orbital interaction is expected to be that between the electrophile's LUMO and the nucleophile's HOMO. The association with the counter-ion lowers significantly the HOMO's energy, thus diminishing its interaction with the electrophile's LUMO; the metallated species have also a rather low energy LUMO, centered on the counter-ion, whose interaction with the HOMO of the carbonyl group could be significant. Thus two orbital interactions have to be considered when dealing with the metallated species, as indicated schematically in Figure 3 of ref 7 for Li. Because the HOMO of the carbonyl group is polarized toward the oxygen atom, this interaction is maximized if the alkali metal and oxygen atoms approach in the transition state. It can be noted that because the metal significantly polarizes the allylic HOMO in the direction of the carbon atom bound to it, and the LUMO

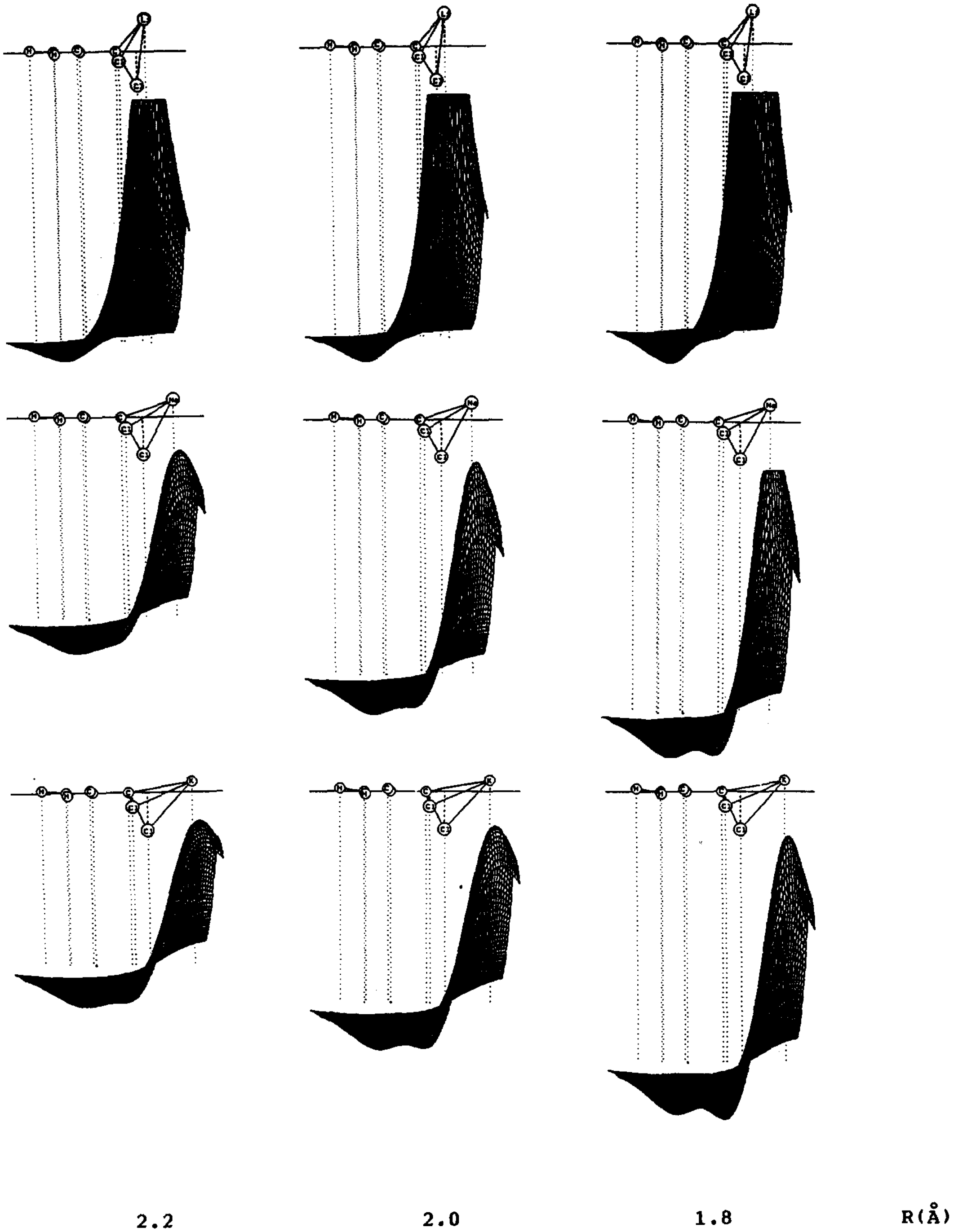


Figure 7

of the carbonyl group is polarized toward the carbon atom, the frontier orbitals would as a consequence interact in a more favourable way, if the electrophile approached the allylic system *via* a four-center transition structure, as found computationally for the attack of formaldehyde to methyllithium.[15] Therefore, for the Na and K dichloro systems, the following factors indicate in a sharp way that an electrophilic attack could be favoured on the carbon atom closer to the counter-ion: the electron distribution and HOMO polarizations just discussed, related to the structural features shown in Figures 2c, 3b and 4b (with the possibility that the counter-ion be involved in the transition structures for the carbonyl addition reaction). On the contrary, for the Li dichloro system the indications obtained from the electrostatic maps oppose those provided by the HOMO polarization. Finally, a different regioselective pattern could be found in the monosubstituted systems. Here P-value ratios are for Li as favourable to a CHCl attack as in the dichloro case, less favourable for Na, but against an α attack for K (Table 2). Electrostatic potential maps for monochloro systems (not shown) are for all cations similar in some respect to those shown for Li in Figure 7, where the repulsive region surrounding the counter-ion is the dominant feature and appears to discourage a *hard* electrophile attack on the substituted carbon. This situation is determined mostly (compare Figure 6) by the geometrical structures.

TABLE 3

Reactions of metallated 3,3-dichloropropene with some carbonyl compounds:[a] CCl_2:CH_2 ratios[b] and yields[c].

Carbonyl compd.	Li[d]	Na[e]	K[f]
PhCHO	15:85 (80)[g]	100:<1 (70)	100:<1 (70)
p-$CF_3C_6H_4CHO$	<1:100 (75)		100:<1 (65)
o-ClC_6H_4CHO	<1:100 (65)		100:<1 (60)
p-ClC_6H_4CHO	<1:100 (73)	100:<1 (68)	100:<1 (67)
o-$MeOC_6H_4CHO$	<1:100 (68)	100:<1 (65)	100:<1 (63)
p-$MeOC_6H_4CHO$	23:77 (75)[g]	100:<1 (60)	100:<1 (65)
o-MeC_6H_4CHO	<1:100 (63)		100:<1 (60)
p-MeC_6H_4CHO	<1:100 (68)	100:<1 (65)	100:<1 (68)

a: 3,3-dichloropropene, 2.5 mmol; carbonyl compound, 2.5 mmol; LDA, 2.5 mmol; THF, 20 ml; T= -95 °C. b: by ^1H n.m.r. on the crude reaction product (±5%). c: in parentheses; isolated product. d: data from ref. 3. e: *t*-BuONa, 3.12 mmol. f: data from ref. 3; *t*-BuOK, 3.12 mmol. g: total yield.

The conclusions of the present study can be compared with the experimental results of some reactions of the metallated 3,3-dichloropropene with various substituted benzaldehydes (Table 3). When lithium is the counter-ion of the *gem*-dichloroallyl anion all the tested carbonyl compounds attack the allylic system with a marked preference for CH_2 terminus. On the contrary, when the same reactions are carried out in the presence of sodium or potassium *tert*-butoxide, the reaction products correspond to an attack at the CCl_2 site. Schlosser[17] and Lochmann[18] have prepared organopotassium compounds by treating organolithium derivatives with potassium alkoxide. Similarly, we assume that working in the presence of sodium and potassium *tert*-butoxide the carbonyl compounds react with *gem*-dichloroallyl-sodium and -potassium, respectively.

Experimental

The apparatus and the reaction procedure for *gem*-dichloroallyl-lithium and *gem*-dichloroallyl-potassium has been previously described.[3] All the reactions of *gem*-dichloroallyl-sodium were likewise carried out under inert atmosphere in flame dried glassware with anhydrous THF. n-Butyllithium and diisopropylamine were purchased from Aldrich, sodium *tert*-butoxide from Fluka, and were sublimated under vacuum (0.1 Torr) prior to the reaction. The carbonyl compounds were commercial and were used without further purification. 3,3-Dichloropropene was synthetized according to the literature.[19] ^1H N.m.r spectra were recorded on a Hitachi Perkin-Elmer R-24B 60 MHz high resolution spectrometer using TMS as internal standard. Mass spectra were recorded at 70 eV with a HP 5970 B mass selective detector connected to a HP 5890 GC (cross-linked methyl silicone capillary column).

Reaction Carried out with LDA in the Presence of Sodium tert-Butoxide. Diisopropylamine (0.25 g, 2.5 mmol) in anhydrous THF (1 ml) was added dropwise with a syringe to a previously cooled (-20 °C) solution of *n*-butyllithium (1.6 ml, *i.e.* 2.5 mmol; 1.6 M solution in hexanes) dissolved in 20 ml of dry THF. After a few minutes the flask was cooled at -95 °C, then sodium *tert*-butoxide (0.30 g, 3.12 mmol) was added and the apparatus allowed to stand for 15 min to equilibrate the temperature. A mixture of 3,3-dichloropropene (0.27 g, 2.5 mmol) and of the desired carbonyl compound (2.5 mmol) in 1.0 ml of anhydrous THF was added dropwise under stirring within 5 min. The reaction mixture was then stirred for 2 h under argon at -95 °C. After the addition of $ClSi(CH_3)_3$ (0.5 ml, 3.9 mmol) the reaction mixture was allowed to reach room temperature, then poured in water. The organic layer was separated and the aqueous one extracted twice with diethyl ether (15 ml). The combined organic phases were washed with brine (10 ml) and dried with anhydrous Na_2SO_4. The solution was condensed under reduced pressure and the residue was analysed by ^1H n.m.r. spectroscopy, in order to establish the CCl_2:CH_2 ratio. All the obtained compounds show ^1H n.m.r. and mass spectra in agreement with those previously reported.[3]

Aknowledgements

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12 The pyramidalization angle τ is computed as the angle between the $C\alpha C\beta$ bond and the normal to the CHCl or CCl_2 plane (a planar structure has $\tau = 90.0°$, while a tetrahedral arrangement gives $\tau = 144.7°$).

13 At the same computational level the CC bond length values for ethane and ethene are 1.542 and 1.320 A respectively.

14 Preliminary computations on this system allowed to discuss its regioselectivity: Angeletti, E.; Baima, R.; Canepa, C.; Degani, I.; Tonachini, G.; Venturello, P. *Tetrahedron* **1989**, *45*, 7827-7834.

15 Kaufmann, E.; Schleyer, P.v.R.; Houk, K.N.; Wu, Y.-D. *J. Am. Chem. Soc.* **1970**, *107*, 5560-5562. The attack of formaldehyde on the α and γ positions of lithium and sodium 1,1-dichloropropenide is under study.

16 Similar maps for Li-difluoropropenide[7] show an α carbon depression deeper than the γ .

17 Schlosser, M.; Hartmann, J. *J. Am. Chem. Soc.* **1976**, *98*, 4674-4676.

18 Lochmann, L.; Lim, D. *J. Organometal. Chem.* **1971**, *28*, 153-158.

19 King, W.H.; Smith, H.A. *J. Am. Chem. Soc.* **1950**, *72*, 3459-3462.