5218 *J. Phys. Chem. A* **2008,** *112,* 5218–5223

A Theoretical Study of Pericyclic Rearrangements Catalyzed by Lithium

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Received: February 7, 2008; Revised Manuscript Received: March 28, 2008

The role of lithium cation in the isomerization from diademane to triquinacene and in the Claisen reaction from phenyl allyl ether to 6-allyl-2,4-cyclohexadienone was analyzed. The nature of the interaction of the lithium ion with the reacting molecules in the transition state was studied using supermolecule and perturbational methods. The aromaticity of the transition state in presence of lithium was compared with that for the same reaction in absence of catalyst, employing tools such as nucleus-independent chemical shift and anisotropy of the induced current density. Our results support that the catalytic effect is caused principally by a more favorable electrostatic interaction of lithium cation with the transition states of both reactions.

Introduction

Lithium is the most polarizing alkaline element. Because of this property, it forms highly polar covalent bonds. Because in carbon−lithium bonds carbon adopts a negative partial charge, it is usual in organic synthesis to employ lithium when a nucleophilic carbon is needed. In the 80s, Braun and Sauer[1] discovered the influence of the system $LiClO_4/Et_2O$ in the most popular pericyclic reaction, the Diels−Alder cycloaddition. Since then, this catalytic system became popular for this kind of reaction.

A curious group of hydrocarbon reactions with peculiar geometries and without a special place to accommodate a Lewis acid catalyst such as the lithium cation got the attention of Stefan Moss and co-workers.[2] In their search of efficient lithium salts less dangerous than $LiClO_4$, they tested the $LiCB_{11}Me_{12}$ salt as catalyst in a series of reactions, the isomerization of diademane to triquinacene being one of them (see Figure 1). Triquinacene was synthesized by Woodward[3] for the first time in 1964, and seven years later De Meijere et al. obtained diademane,[4] which melts near to 100 °C to give triquinacene. It is a ${}_{\pi}2_s + {}_{\pi}2_s + {}_{\pi}2_s$ cycloreversion allowed by the principle of orbital symmetry conservation.[5] It is important to remark that the reactivity of diademane depends on the type of catalyst:[6] in the presence of Ag(I) diademane goes to triquinacene but with Au(I) goes to snoutene; moreover, Cu(I) catalyzes both reactions.

The effect of this catalyst was also proved in a classical Claisen reaction,[2] from phenyl allyl ether to ketone (6-allyl-2,4-cyclohexadienone). The experimental data show that this reaction is possible in absence of catalyst, but it needs high temperatures. The catalyst allows to perform the same reaction in saturated solution of benzene in less time at lower temperatures. Contrary to diademane, a molecule like phenyl allyl ether has a “typical” location to coordinate with a Lewis acid: the oxygen atom.

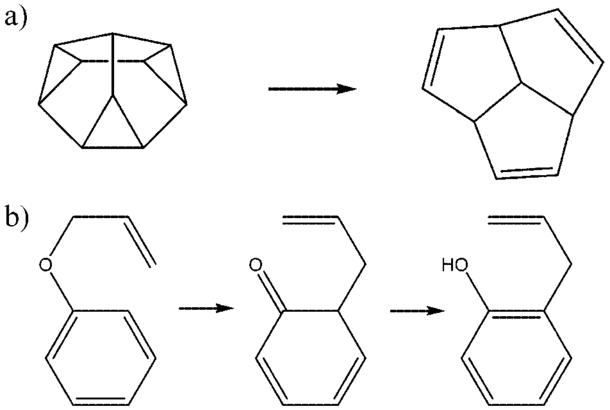

Figure 1. The two pericyclic reactions catalyzed by lithium studied in this work: (a) diademane to triquinacene and (b) phenyl allyl ether to 6-allyl-2,4-cyclohexadienone and its subsequent tautomerization.

In the present work the role of lithium ion as a catalyst is analyzed by studying the nature of the lithium–molecule interaction: is it just an electrostatic effect as we think at a first glance or is there any other effect? It is well-known that pericyclic reactions proceed by means of an aromatic transition state, so the presence of the lithium cation can also modify the aromaticity of the transition state, changing the barrier for the reactions. As magnetic properties are a useful tool to assess the degree of aromaticity of transition states of pericyclic reactions[7] the aromaticity in the transition state was calculated for each reaction in the presence and absence of lithium by different magnetic-based procedures to know if the catalysis is partly due to an increase of aromaticity. The comparison between both reactions allows checking the effect of lithium ion over the reaction depending whether it coordinates to a place not directly involved in the reaction (the oxygen atom in Claisen reaction) or to a region where the most important charge reorganization takes place (diademane to triquinacene case).

Computational Details

Geometries of all stationary points were fully optimized at the B3LYP/6-31G(d,p) level and characterized as minima or

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10.1021/jp801130s CCC: $40.75

saddle points by analytic second-derivative computation of harmonic vibrational frequencies. B3LYP[8] combines the Slater exchange functional corrected by Becke with the correlation potential of Vosko, Wilk, and Nusair corrected by Lee, Yang, and Parr. Next, polarized continuum model (PCM)[9] calculations with benzene as solvent were used to reproduce the experimental conditions. The reaction mechanisms were proved by performing intrinsic reaction coordinate (IRC)[10] calculations at the B3LYP/6-31G(d,p) level in the gas phase.

Magnetic properties were determined by computing the shielding tensors at B3LYP/6-31G(d,p) level using the continuous set of gauge transformations (CSGT) method developed by Keith and Bader.[11] Two different indices were employed:

Nucleus-independent chemical shift (NICS), introduced by Schleyer,[12] is a useful tool to quantify the aromaticity, and it is directly related to the chemical shift in vacuum. NICS values were also calculated employing the CSGT method.

On the other hand, the anisotropy of the current-induced density (ACID) method was implemented by Herges.[13] The current density is a vectorial field obtained by calculating the current induced by an external magnetic field in each point of the space. The anisotropy is a scalar field that can be represented using isosurfaces. Projecting over them the density current vectors, the intensity and direction (which reveals the paratropic or diatropic nature of the current) can be analyzed.

The interaction energy between the molecule and the lithium cation was obtained by the supermolecule method. Therefore, the interaction energy was calculated as the difference between the complete energy of the whole system and the fragments that compound the system (Li^+ and the reacting molecule). Interaction energies were corrected from basis set superpositiong error (BSSE) by employing the counterpoise method.[14] The main advantage of supermolecule method is its simplicity, but it offers little information about the physical nature of the interaction (we only obtain a global value).

Perturbational methods calculate the interaction energy as a sum of contributions, which can be assigned to different physical phenomena. As only an approximate analysis of the different contributions to the interaction energy was intended, the intermolecular perturbation theory (IMPT) method[15] was used for calculations. IMPT is based on the HF wave functions of the monomers and allows to estimate basic contributions to the interaction energy to second order (exchange, electrostatic, induction, charge transfer, and dispersion). Taking into account the nature of the systems studied the attention was focused on electrostatic and induction contributions.

All geometry optimizations and subsequent frequency calculations were performed with Gaussian03 software package.[16] IMPT calculations were performed with CADPAC,[16] and ACID was computed with the program developed by Dr. Herges.[13]

Results and Discussion

Reactivity in Absence of Catalyst. Figure 2 shows the two studied rearrangements in absence of lithium cation.

The thermal isomerization of diademane to triquinacene is a concerted process with an experimental activation barrier about ~28 kcal/mol.[17] Triquinacene, with its three C−C double bonds in fixed positions, was initially considered by Liebman and coworkers[18] as a possible aromatic compound, but its heat of formation does not reveal the expected effect of aromatic stabilization. Later, several experiments and calculations ruled out this doubt.[19] As with any pericyclic reaction, the isomerization occurs through an aromatic transition state.[20]

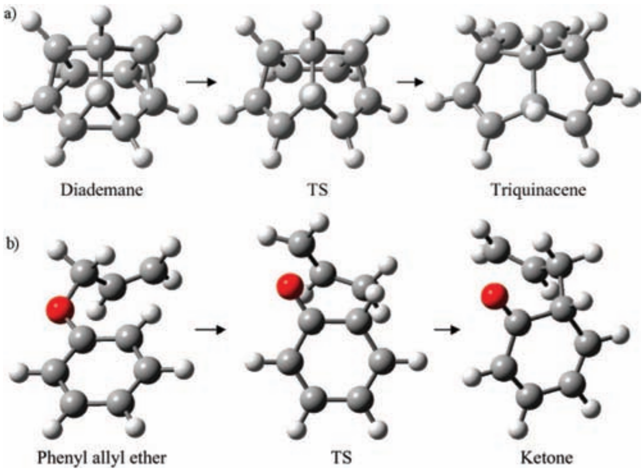

Figure 2. Diademane to triquinacene (a) and phenyl allyl ether to ketone (b) reactions in absence of catalyst, as obtained at the B3LYP/6-31G(d,p) level.

TABLE 1: Electronic Energies without and with Zero-Point energy (ZPE) Correction in Atomic Units and Relative Electronic Energy in kcal/mol at the B3LYP/6-31G(d,p) Level in the Gas Phase.

	E (au.)	E_{ZPE} (au.)	ΔE_{ZPE} (kcal/mol)
diademane	−386.98342	−386.81197	0.00
TS_{diad}	−386.93550	−386.76813	27.50
triquinacene	−387.03531	−386.86530	−33.46
phenyl allyl ether	−424.17889	−424.01251	0.00
TS_{ether}	−424.11582	−423.95219	37.85
ketone	−424.16060	−423.99531	10.79

The energy barrier at the B3LYP/6-31G(d,p) level in gas phase is shown in Table 1. Even in the gas phase, the result (27.50 kcal/mol) is in good agreement with the experimental results. The transition state has an imaginary frequency of ~800 cm^{-1}, and it shows C_{3v} symmetry, as the reactant and the product of the reaction. Formally, the rearrangement resembles three C=C double bonds, which form a cyclohexane. The rigidity of diademane allows the reaction to occur in the same plane, leading to a slightly enlargement of the geometric base of the diademane as the reaction proceeds to triquinacene.

The reaction from phenyl allyl ether to 6-allyl-2,4-cyclohexadienone has a significant barrier near 38 kcal/mol (see Table 1) as calculated at the B3LYP/6-31G(d,p) level. A temperature about 200 °C is needed to perform this reaction.[2] It is also remarkable that this Claisen reaction itself is not exothermic; the "real" product in solution is the enol, product of the tautomerization of the ketone. In the present work just the pericyclic reaction itself was studied without consideration of the subsequent enol formation. Formally, there is a σ bond that is moving from the oxygen to the C_6 of the benzene. The transition state has an imaginary frequency of ~354 cm^{-1}, which corresponds to the breaking of the O−C bond and the formation of the new C−C bond.

Reactions Catalyzed by Lithium. In the isomerization of diademane, there is no special place to locate a Lewis acid since there are no heteroatoms in the starting system, and no double bonds are present for establishing a cation−π interaction. The structure of the molecule remembers the shape of an umbrella, and it is logical to think that the lithium cation should go centered under this structure (see Figure 3). This situation allows an interaction with the π electrons as the reaction proceeds and conserves the symmetry along all the reaction. The geometric deformation due to the cation interaction is very small (only a

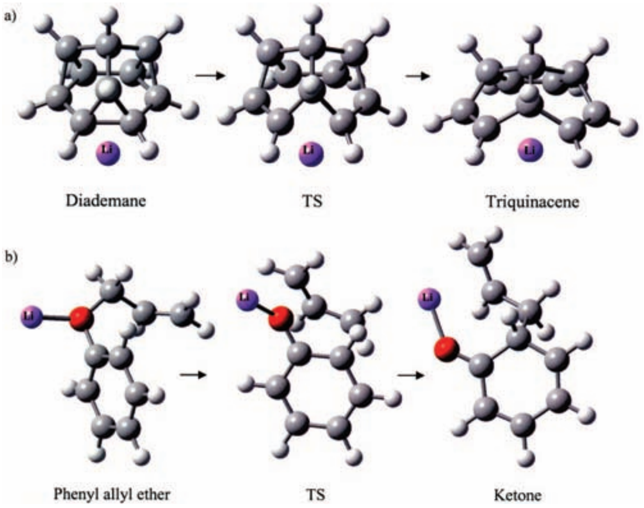

Figure 3. Diademane to triquinacene (a) and phenyl allyl ether to ketone (b) catalyzed by lithium cation B3LYP/6-31G(d,p) results.

TABLE 2: Energies for the Catalyzed Reactions in the Gas Phase and in Benzene Solution (PCM method) at the B3LYP/6-31G(d,p) Level

	ΔE_{ZPE} (kcal/mol)	ΔE_{ZPE} (solv) (kcal/mol)	ΔH_{rel} (solv) (kcal/mol)	ΔG_{rel} (solv) (kcal/mol)
diademane + Li^+	0.00	0.00	0.00	0.00
TS_{diad} + Li^+	14.77	16.74	16.91	16.65
triquinacene + Li^+	−55.46	−36.28	−35.37	−37.36
phenyl allyl ether + Li^+	0.00	0.00	0.00	0.00
TS_{ether} + Li^+	17.34	18.82	18.40	20.85
ketone + Li^+	−12.33	−4.43	−4.76	−2.57

slight opening in the hexagonal base of the molecule). The lithium cation keeps the same position on the C_3 symmetry axis during the isomerization. The IRC obtained at the B3LYP/6-31G(d,p) level confirms that the transition state thus located corresponds to the desired process. The energy values in gas phase at the same level of calculation are shown in Table 2. The energy barrier decreases considerably: from 27.50 to 14.77 kcal/mol, almost a 50% decrease with respect to the value in absence of catalyst. The same calculations were done with PCM method in benzene solution, and the values remain more or less similar (see Table 2). Some thermodynamic data are also shown in Table 2 for this reaction, which shows only small differences with respect to the electronic energy, indicating that entropy does not play an important role in this case.

In the Claisen reaction, there is an oxygen atom that will be the place where the lithium can preferentially bond with the system. One more time, employing the catalyst allows reduction of the energy barrier (17.34 kcal/mol) by 50% with respect to the same reaction in absence of catalyst (see Table 2). Also the pericyclic reaction itself is now exothermic in the presence of lithium ion. As in the diademane case, the IRC confirms the transition state to correspond to the desired reaction, and the PCM calculations (Table 2) present no significant differences in the barrier, though the product is not so stable in benzene solution. However, the reaction is still exothermic in solution.

Nature of the Catalysis. We are also interested in knowing if the acceleration of these reactions is due to purely electrostatic effects or on the contrary it depends on other factors such as changes on the aromaticity of the transition states or a larger polar character of the reaction.

To estimate these effects, in a first approximation, Li^+ was substituted by a positive charge and by its valence orbitals.[21] Table 3 shows the effect in the energy barrier of replacing Li^+ by: (a) its valence orbitals, (b) a positive charge, and (c) a dummy atom carrying the basis set of the ion. To do part a is just to enlarge the basis set a few since the ion is not present though basis function associated to it still remain; to do part b is a simple way to look qualitatively if the effect is purely electrostatic. It is worth noting that the values of the 1,3 and 2,4 rows are very similar for the two reactions. This seems to indicate that the catalysis is principally due to an electrostatic effect.

TABLE 3: Lithium Cation Replaced by Its Valence Orbitals, a Positive Charge and a Dummy Atom for (a) Diademane to Triquinacene; (b) Phenyl Allyl Ether to Ketone (Values Do Not Include ZPE Correction)

(a) diademane to triquinacene	*E* diademane (au.)	*E* TS_{diad} (au.)	ΔE (kcal/mol)
without catalyst	−386.98342	−386.93550	30.07
with catalyst	−394.34439	−394.31772	16.73
valence orbitals	−386.97509	−386.92943	28.65
positive charge	−387.06752	−387.03712	19.08
dummy atom	−386.97959	−386.93315	29.14
(b) phenyl allyl ether to ketone	***E* phenyl allyl ether (au.)**	***E* TS_{ether} (au.)**	**ΔE (kcal/mol)**
without catalyst	−424.17889	−424.11582	39.58
with catalyst	−431.53242	−431.50242	18.83
valence orbitals	−424.16313	−424.10887	34.05
positive charge	−424.25305	−424.22725	16.19
dummy atom	−424.16775	−424.11215	34.89

TABLE 4: Results for the Interaction Energy Calculated with the Supermolecule Method

	ΔE_{int} (kcal/mol)	$\Delta(\Delta E_{int})$ (kcal/mol)	ΔE_{int} deformation included (kcal/mol)	$\Delta(\Delta E_{int})$ deformation included (kcal/mol)
diademane	−48.61	0.00	−47.89	0.00
TS_{diad}	−60.23	−11.62	−57.97	−10.08
triquinacene	−50.63	−2.02	−48.68	−0.78
phenyl allyl ether	−47.49	0.00	−44.75	0.00
TS_{ether}	−62.61	−15.12	−58.97	−14.23
ketone	−68.36	−20.88	−64.46	−19.71

TABLE 5: Interaction Energy Decomposition for the Lithium Complexes as Obtained with the IMPT Method with the 6-31G(d,p) Basis Set

	E diademane (kcal/mol)	*E* TS_{diad} (kcal/mol)	ΔE (kcal/mol)
electrostatic energy	−27.47	−41.78	−14.31
repulsion energy	15.93	19.62	3.69
induction energy	−33.39	−33.69	−0.30
charge transfer energy	−4.01	−6.11	−2.10
dispersion energy	−1.02	−1.07	−0.05
	***E* Phenyl allyl ether (kcal/mol)**	***E* TS_{ether} (kcal/mol)**	**ΔE (kcal/mol)**
electrostatic energy	−37.61	−58.78	−21.17
repulsion energy	12.99	17.64	−4.65
induction energy	−27.34	−25.19	2.15
charge transfer energy	−2.22	−1.92	0.30
dispersion energy	−0.63	−0.80	−0.17

Interaction energies were calculated employing the supermolecule method, the results being shown in Table 4. The interaction was calculated without and with deformation. The first one is the result of subtracting the energy of the whole molecular system and the energy of the fragments A and B (the molecule and the cation) with the same geometry they have in

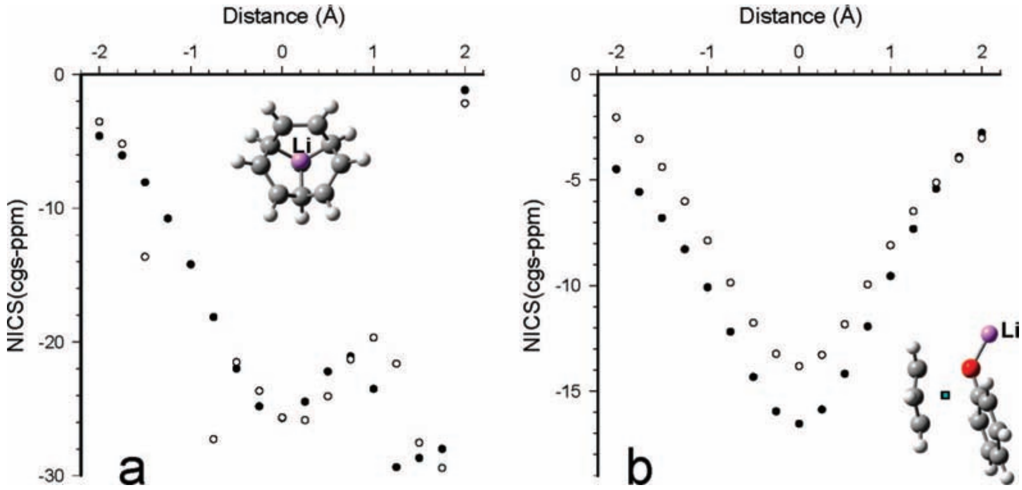

Figure 4. NICS values along an axis perpendicular to the plane of the atoms that take part in the reaction for: (a) diademane to triquinacene and (b) phenyl allyl ether to ketone. Black points are without catalyst, and white points are with catalyst. The 0 Å value corresponds to the plane containing the ring critical point. The *z* axis, going from the reader to the paper is perpendicular to that plane and passes trough the ring critical point, located just below Li^+ in reaction a and marked as a square for the Claisen reaction.

the complex. The second one is the result of taking into account the geometry change of the molecules when the complex is formed. This "deformation energy" can be calculated as

$$E_{\mathrm{def}} = E_{\mathrm{A}}^{\mathrm{com}}(\mathrm{A}) + E_{\mathrm{B}}^{\mathrm{com}}(\mathrm{B}) - E_{\mathrm{A}}^{\mathrm{isol}}(\mathrm{A}) - E_{\mathrm{B}}^{\mathrm{isol}}(\mathrm{B}) \qquad (1)$$

where $E^{\mathrm{com}}{}_{\mathrm{A}}(\mathrm{A})$ is the energy of the fragment A with its own basis set in the geometry of the complex, and $E_{\mathrm{A}}{}^{\mathrm{isol}}(\mathrm{A})$ is the energy of A if it was an isolated molecule (the same for B). In the case of transition states, deformation energies were computed with respect to the transition state in absence of lithium ion.

In the diademane reaction, the interaction energy in the transition state is remarkably higher than in the reactant. The same behavior is observed in the Claisen reaction, with energy differences between reactant and TS even larger than in the diademane case. Therefore, it seems to be a clear correlation between the decrease of energy barriers and the increase of the lithium interaction in the transition state. That is, the more favorable interaction of Li^+ with the transition state as compared with respect to reactant is the main responsible of the decrease of the energy barrier and therefore of the catalytic effect. This fact helps to justify the notable decrease in the activation energy in presence of lithium, and probably we can say that lithium seems to be more effective as catalyst in a "classical" acid Lewis position.

To get insight into this subject, an interaction energy decomposition analysis was performed by means of IMPT calculations. With the IMPT method we can assign a physical interpretation to each component of the energy. As observed in Table 5, the main attractive contributions both in reactant and in transition states are of electrostatic and inductive nature, as expected for this kind of complex. However, the only significant changes when going from reactant to transition state correspond to electrostatic energy, which shows an important increase in intensity, which roughly corresponds to the decrease in energy barriers, whereas induction contributions remain almost unchanged. All other energy contributions show only marginal changes. Therefore, though the main contributions to the interaction energy are, as expected, of electrostatic and inductive nature, only the electrostatic contribution changes noticeably when going from reactant to transition state by a magnitude that roughly corresponds to the decrease in energy barriers, suggesting that it is this reinforcement of electrostatic interactions the main responsible of the catalytic effect.

Aromaticity of the Transition State. As the two studied reactions are pericyclic and, in consequence, they proceed through an aromatic transition state, changes in aromaticity were checked to determine whether the presence of lithium ion gives way to a different mechanism without passing through an aromatic transition state or whether the main characteristics of pericyclic reactions are kept instead. The aromaticity of the transition state was estimated by means of magnetic properties, NICS and ACID, were those used in this work.

Sign and magnitude of the NICS values are related to the aromaticity of the transition state, since especially negative values suggest an aromatic behavior. NICS was calculated along a line passing through the ring critical point (3,+1) as determined with Bader's atoms in molecules theory,[22] which roughly relies in the plane defined by the atoms involved in the reaction (the line where NICS is obtained is perpendicular to this plane). Figure 4 shows the variation of NICS in the transition states for the reactions studied. It can be observed that for the diademane to triquinacene reaction the most significant values are around −20/−25 cgs/ppm. Those values correspond to points in the plane and just over and below it: it is usual to measure NICS in the center of the aromatic rings (NICS(0)) and also at a reasonable distance of the plane (1 Å, NICS (1)).[23a,b] So, the most important points are those in which the plot corresponds with the minimum of the central part of the curve. It is also remarkable that the values of the noncatalyzed reaction are slightly more negative than the catalyzed ones, though we believe the effect is not as high as to establish that a significant decrease in aromaticity occurs, affecting the energy barrier.[23c] Figure 4 also shows that for the catalyzed reaction several points greatly depart from the tendency exhibited by the noncatalyzed reaction. The reason for this behavior is that these points correspond to the region occupied by the lithium ion. For the Claisen rearrangement a similar analysis can be done, the behavior being similar for the reactions with and without catalyst, exhibiting clearly negative NICS values near the plane of the aromatic ring. In this case, no points departing from the general trend are observed for the catalyzed reaction since the line where NICS was calculated is far apart from lithium ion.

ACID is a scalar field, and represents the delocalized electron density. Plotting current density vectors onto ACID isosurfaces allows determining how intense the currents are and which is

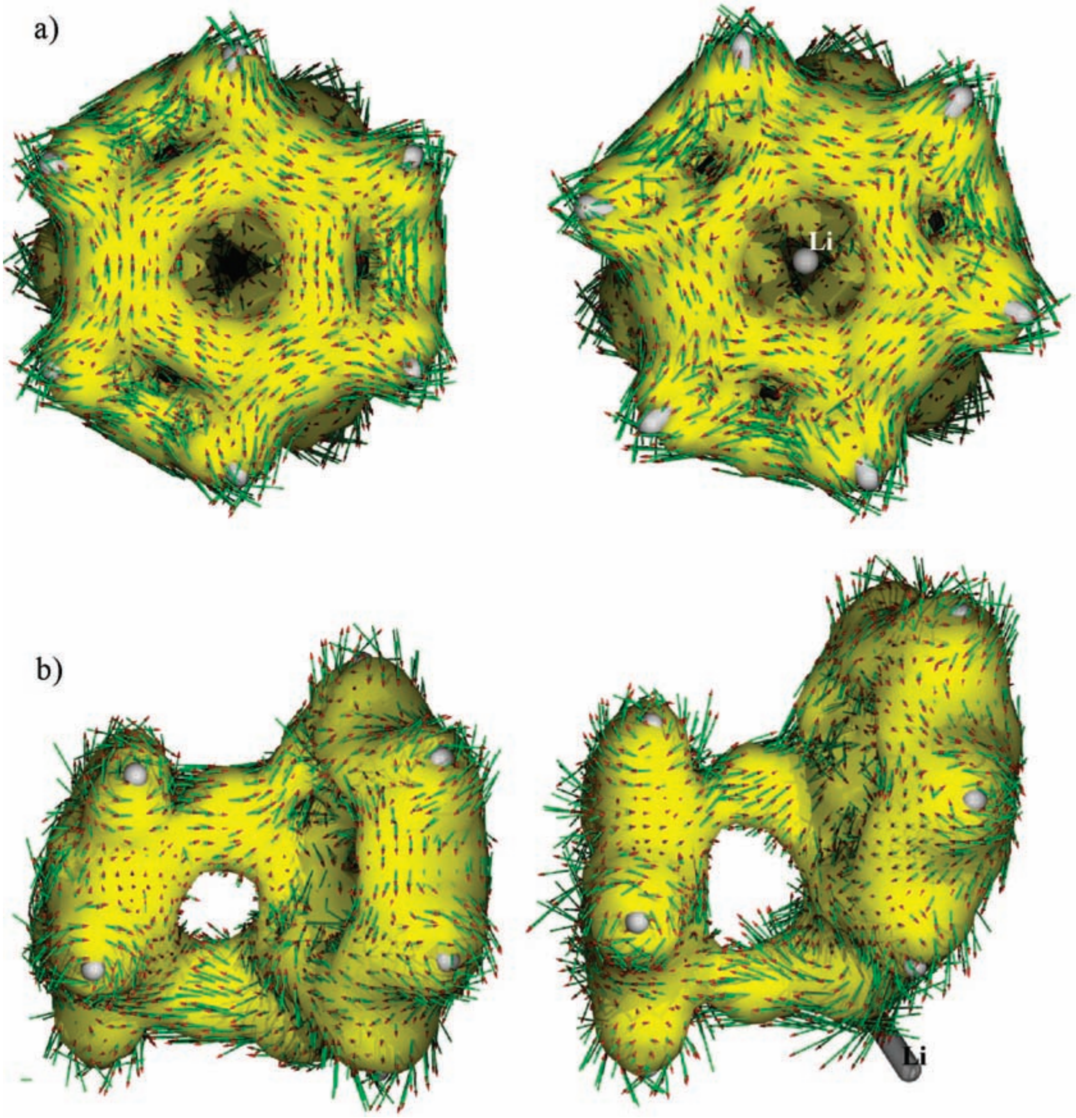

Figure 5. ACID plots for the transition states of (a) diademane to triquinacene isomerization and (b) phenyl allyl ether to ketone. Isosurface value = 0.03. Figures on the left are without the lithium ion; figures on the right are with the lithium ion.

their direction (paratropic or diatropic)(^{24}). In the diademane case, the results lead to the same conclusion as NICS (see Figure 5): we can observe an aromatic diatropic ring current in both cases, with and without catalyst. The degree of delocalization can also be quantified by means of the critical isosurface value (CIV) in each case. A smaller CIV indicates a weaker delocalization. CIVs for the TS with and without catalyst are considerably high in diademane to triquinacene reaction: 0.072 and 0.081, respectively. These two values are close, reinforcing the conclusions mentioned before regarding the marginal influence of lithium ion on aromaticity. For the Claisen reaction diatropic currents are also observed, though weaker than in the diademane case, especially for the catalyzed reaction. CIV's amount to 0.043 and 0.072 with and without catalyst, respectively. Therefore, though the reaction without catalyst exhibits similar values to those observed for the diademane to triquinacene case, the presence of lithium ion produces a significant decrease in CIV, although the value is still large enough to consider the catalyzed reaction as pericyclic (the observed ring current is diatropic). This behavior is also in agreement with that observed from NICS values.

Conclusions

In accordance with the results, the lithium cation employed as catalyst reduces at least in a 50% the energy barriers of the studied reactions. The decrease in the energy barrier is due to an enhanced electrostatic interaction in transition states with respect to reactants, as shown by different calculations. Finally, no significant aromaticity changes were observed in presence of lithium cation, the mechanism remaining as typically pericyclic.

Acknowledgment. The authors thank the Ministerio de Educación y Ciencia (CTQ2006-11087/BQU). We are also thankful to the Centro de Supercomputación de Galicia (CESGA) for the use of their computers and to Dr. Herges for providing the ACID program. M.M.M.-C. thanks the Xunta de Galicia and its Maria Barbeito program for financial support.

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JP801130S