Theoretical evidence for stereoselective lithiations of 2-alkoxy-1,1-diiodo-1-alkenes
An ab initio study

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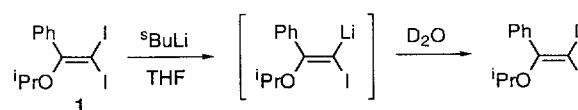[c] *Organisch-Chernisches Institut, Universität Zürich, CH-8057 Zürich, Switzerland*

Abstract

Ab initio calculations with complete geometry optimization are reported for monomeric Z- and E-2-methoxy-1-iodo-1-lithio-2-phenyl-1-alkenes. All the stationary points are true local minima on the energy surfaces. The structural data of the lithioalkenes show clear-cut evidence for the Li–Phenyl interaction in Z-isomer and the Li–O chelation in E-isomer in gas-phase. Based on the ab initio energies, Li–Phenyl interaction should be less relevant than Li,O chelation. Both effects are absent when coordination by solvent (water) is accounted. Inclusion of solvation by solvent continuum model (IPCM) seems essential to rationalize the experimental results. © 1997 Elsevier Science S.A.

1. Introduction

The development of stereoselective functionalizations is always an important task in organic chemistry. We have recently described the preparation of a 2-alkoxy-1-iodo-1-lithio-1-alkene by treatment of a 2-alkoxy-1,1-diiodo-1-alkene **1** with organolithium compounds in tetrahydrofuran followed by electrophile addition (Scheme 1) [1]. The structure of the β-functionalized lithioalkene is not well defined due to its carbenoid nature, but its chemical behavior suggests a *trans* relationship for the lithium and the alkoxy groups. The process should be thermodynamically controlled since the solution of the lithiated vinyl iodide in THF is stable at −20°C and, even, it can be partially trapped by electrophiles at room temperature without detection of

E-isomer [1]. At first glance, it might be expected that favorable interactions between lithium and the alkoxy groups should be the controlling effect to afford the other stereoisomer. In fact, this stereocontrol has been observed in analogous systems [2]. In order to explain the formation of the unexpected stereoisomer, we have carried out ab initio calculations. The obtained results are described below.

Ab initio calculations were performed by using the Gaussian94 program package [3]. The molecular geometries were optimized without any molecular symmetry constraint at the Hartree-Fock self-consistent field (HF) level of theory with the standard split-valence 3-21G

Scheme 1.

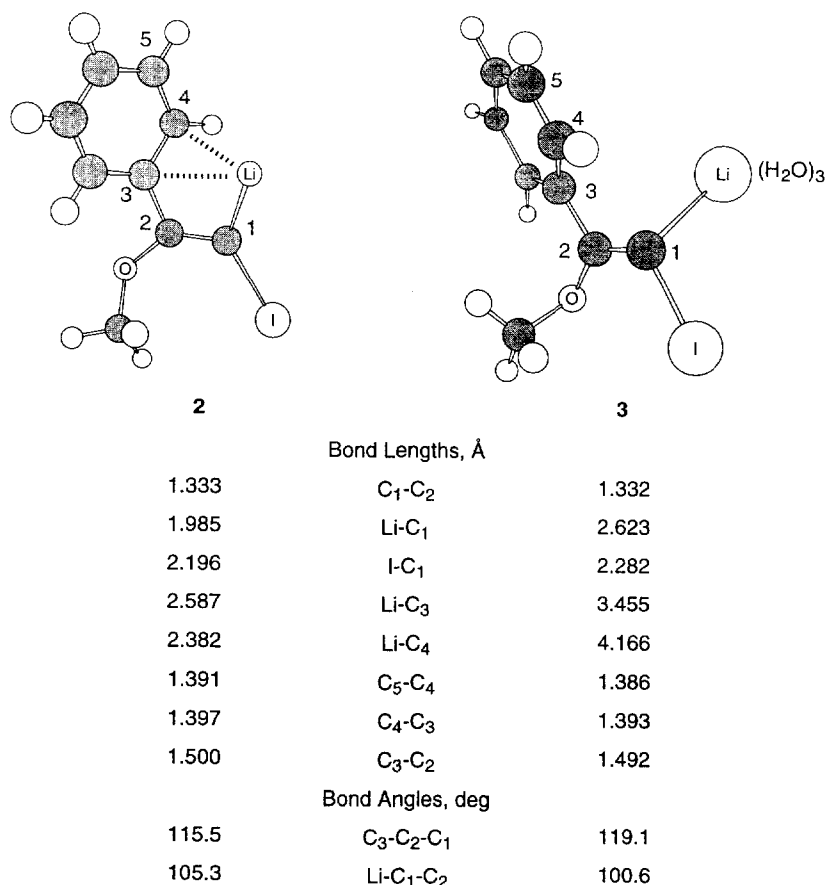|	Bond Lengths, Å	
	2	**3**
1.333	C_1-C_2	1.332
1.985	Li-C_1	2.623
2.196	I-C_1	2.282
2.587	Li-C_3	3.455
2.382	Li-C_4	4.166
1.391	C_5-C_4	1.386
1.397	C_4-C_3	1.393
1.500	C_3-C_2	1.492
	Bond Angles, deg	
115.5	C_3-C_2-C_1	119.1
105.3	Li-C_1-C_2	100.6

Fig. 1. Computer plot and selected geometrical parameters of the HF/3-21G optimized structures for nonsolvated, **2**, and trisolvated, **3**, Z-1-iodo-1-lithio-2-methoxy-2-phenyl-1-ethene.

basis set using Schlegel's analytical gradient procedure [4]. The optimized structures were characterized as minima by analytic frequency calculations. In order to obtain reliable relative energies, additional single-point on the HF/3-21G geometries were performed using the 6-31G(d) basis set [5–7] for C, Li, O and H and the effective core potential (ECP) by Wadt and Hay [8] augmented by a set of six d-type polarisation functions for I [1] [9] at the MP2 level [10,11]. This valence basis set, hereafter referred to as SV(d), seems good balanced for all atoms and includes relativistic corrections by using ECP for I. Furthermore, the MP2/SV(d)//HF/3-21G level may provide relative energies that would be quite accurate for the Li–O chelation [12]. Finally, for a complementary modeling of solvation effect [13], single-point calculations were carried out with the isodensity surface polarized contin-

uum model (IPCM), as implemented in Gaussian94 [3], using the dielectric constant of THF ($\varepsilon = 7.58$).

2. Materials

To perform these calculations in a reasonable amount of computer time, 1-iodo-1-lithio-2-methoxy-2-phenyl-1-ethene (nonsolvated and solvated with three water molecules) was selected as our working model and we considered monomeric Z- and E-1-lithio-1-alkenes [14]. [2,3] Figs. 1 and 2 show the most important struc-

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[1] The valence basis set is (21/21/1). The exponent for d-type polarisation functions is 0.266.

[2] It has been recently crystallized and analyzed, a lithiated vinyl chloride in the presence of tetrahydrofuran and tetramethylethylene-diamine revealing a monomeric solvated structure.

[3] Preliminary calculations on 1-iodo-1-lithioethene solvated with water molecules at the MP2/SV(d)//HF/SV(d) level indicate that monomeric structure should be 16.8 kcal/mol more stable than dimeric.

Bond Lengths, Å

1.324	C_1-C_2	1.328
2.003	Li-C_1	2.410
2.171	I-C_1	2.289
1.835	Li-O	3.254
1.490	O-C_2	1.448

Bond Angles, deg

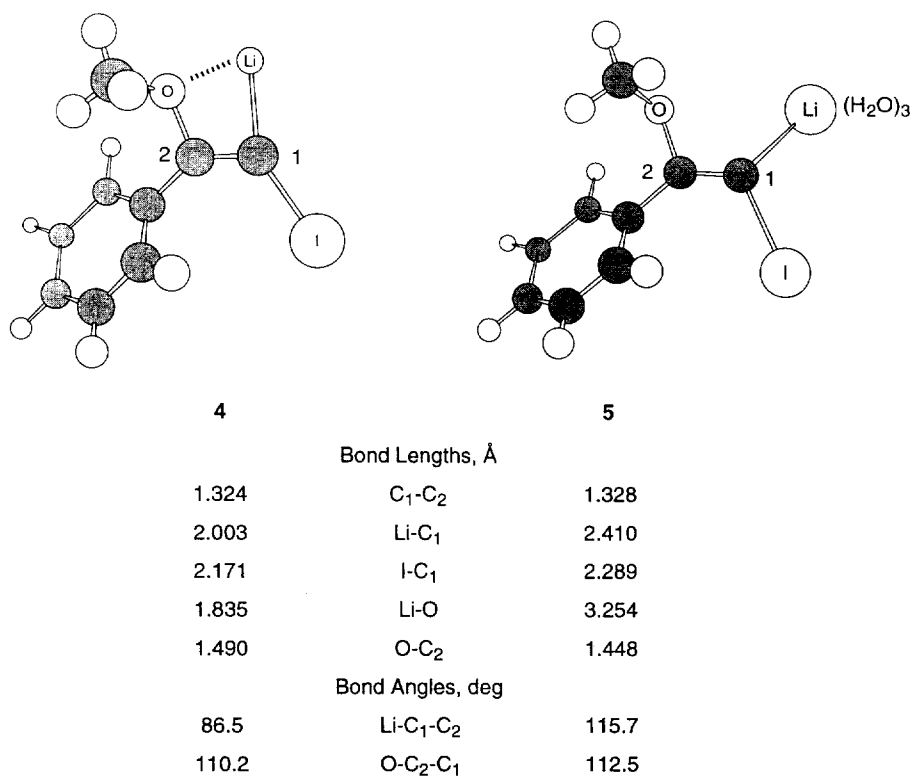| 86.5	Li-C_1-C_2	115.7
110.2	O-C_2-C_1	112.5

Fig. 2. Computer plot and selected geometrical parameters of the HF/3-21G optimized structures for nonsolvated, **4**, and trisolvated, **5**, *E*-1-iodo-1-lithio-2-methoxy-2-phenyl-1-ethene.
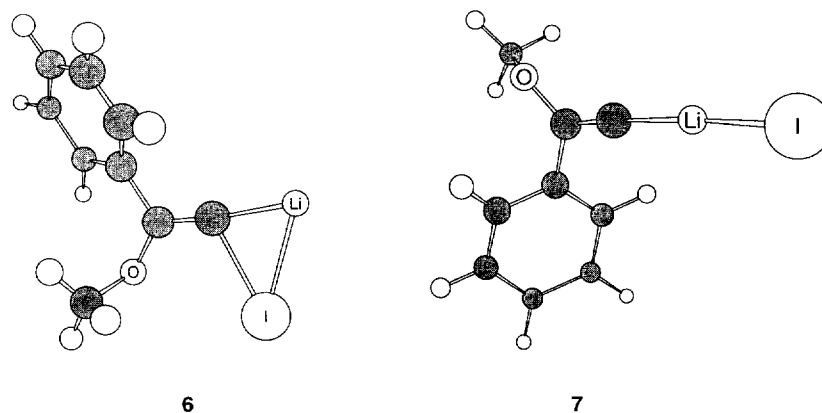

Fig. 3. Computer plot of the HF/3-21G optimized structures for nonsolvated **6** and **7** minima.

Table 1
Absolute energies (+438.0) in hartrees, relative energies in kcal/mol (in parentheses)

	2	**4**
HF/SV(d)//HF/3-21G	−0.892634 (5.4)	−0.901305 (0.0)
MP2/SV(d)//HF/3-21G	−2.335325 (6.0)	−2.344937 (0.0)
HF/SV(d)//HF/3-21G including IPCM solvation[a]	−0.947340 (−12.9)	−0.926767 (0.0)
MP2/SV(d)//HF/3-21G including IPCM solvation[a]	−2.383350 (−11.7)	−2.364703 (0.0)

[a]Calculated dipole moments: 7.5 (**2**) and 6.9 (**4**) debyes.

Table 2
Absolute energies (+666.0) in hartrees, relative energies in kcal/mol (in parentheses)

	3	5
HF/SV(d)//HF/3-21G	−0.114865 (3.8)	−0.120935 (0.0)
MP2/SV(d)//HF/3-21G	−2.109649 (4.5)	−2.116820 (0.0)
HF/SV(d)//HF/3-21G including IPCM solvation[a]	−1.038926 (−4.4)	−1.031871 (0.0)
MP2/SV(d)//HF/3-21G including IPCM solvation[a,b]	−3.033710 (−3.7)	−3.027756 (0.0)

[a] Calculated dipole moments: 5.7 (3) and 4.1 (5) debyes.
[b] From IPCM solvation at the HF/SV(d)//HF/SV(d) level.

tural data of the optimized geometries for the isomers 2–3 and 4–5, respectively. There were also located two other nonsolvated structures, 6 and 7 (see Fig. 3), but they lead to 3 and 5, respectively, when the lithium atom is solvated with water.

3. Discussion

It is noteworthy that there are significant differences between the Z- and E-1-lithio-1-alkenes. In the nonsolvated Z-isomer, 2, the $Li-C_3$ and $Li-C_4$ distances (2.587 and 2.382 Å, respectively) indicate a Li–Phenyl interaction [15–17]. On the other hand, the Li–O and $O-C_2$ distances in 4 (1.835 and 1.490 Å, respectively) and the $Li-C_1-C_2$ bond angle (86.5°) indicate a Li–O chelation. These interactions were not observed in trisolvated structures. Thus, in the solvated Z-isomer, 3, the calculated $Li-C_3$ and $Li-C_4$ distances are 3.455 and 4.166 Å, respectively, while in the solvated E-isomer, 5, the Li–O and $O-C_2$ distances are 3.254 and 1.448 Å, respectively, and the $Li-C_1-C_2$ bond angle is 115.7°.

The calculated energies for 2 and 4 are summarized in Table 1. According to our calculations, at the HF/SV(d)//HF/3-21G and MP2/SV(d)//HF/3-21G levels, the E-isomer, 4, (with a cis relationship between lithium and methoxy groups) should be more stable than the Z-isomer, 2, by 5.4 and 6.0 kcal/mol, respectively, in disagreement with the experimental results. These gas-phase calculations suggest that Li–O chelation should be more relevant than Li–Phenyl interaction. However, the solvation, which plays an important role in organometallic chemistry, has not been accounted. After coordination by solvent (water) molecules, the E-isomer, 5, should be more stable than the Z-isomer, 3, by 3.8 and 4.5 kcal/mol at the HF/SV(d)//HF/3-21G and MP2/SV(d)//HF/3-21G levels, respectively (see Table 2). Inclusion of solvation by IPCM method ($\varepsilon = 7.58$) reverses this order and makes 2 and 3 the most stable stereoisomers (see Tables 1 and 2: 12.9 and 4.4 kcal/mol at the HF/SV(d)//HF/3-21G level and 11.7 and 3.7

kcal/mol at the MP2/SV(d)//HF/3-21G level, respectively) in line with experimental findings. These results can be explained considering that the less polar 4 and 5 (see Table 2) have a weaker, less stabilizing interaction with the solvent than 2 and 3, respectively. On the other hand, looking at the relative stabilization produced by the IPCM solvation, it derives that nonsolvated and solvated structures have different responses to the continuum solvation model. Thus, both factors, coordination by solvent and solute–continuum interaction, should be taking into account for a good description of organolithium chemistry in solution.

4. Conclusion

In conclusion, the present theoretical study provides evidence of Li–Phenyl interactions and Li–O chelation in Z- and E-2-alkoxy-1-iodo-1-lithio-2-phenyl-1-alkenes in gas-phase. The interaction between the lithium and the phenyl groups is less relevant than Li–O chelation. Both effects are absent when coordination by solvent (water) molecules is accounted. Inclusion of solvation by solvent continuum model seems essential for a good agreement between the ab initio calculations and the experimental results. The present work could serve as an example of the limitations of calculations of gas-phase and solvated models.

Acknowledgements

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