Ab Initio Comparative Study of the Additions to the Carbon and Oxygen of Acetaldehyde Lithium Enolate by Formaldehyde and Ketene

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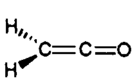
Abstract: Ab initio (3-21G) calculations of the reaction of ketene (**1**) and formaldehyde (**4**) with the lithium enolate of acetaldehyde (**5**) show that in both cases the lithium cation coordinates both oxygens in the complex, the transition structures, and the products. Reaction at carbon of **5** by **1** and **4** proceeds from the initial complexes via half-chair conformations, with activation energies of 6.7 and 1.9 kcal/mol, respectively, and with overall exothermicities of 41.9 and 40.2 kcal/mol, respectively, consistent with a recent thermochemical study. Reaction at oxygen of **5** by **1** and **4** proceeds from the initial complexes via planar four-centered transition structures with activation energies of 5.5 and 5.0 kcal/mol, respectively, and with overall exothermicities of 27.7 and 29.5 kcal/mol, respectively. Thus $CH_2{=}O$ (**4**) has a kinetic preference for reaction at carbon of $CH_2{=}CHOLi$ (**5**), whereas $CH_2{=}C{=}O$ (**1**) is less reactive than **4** but has a slight kinetic preference for reaction at oxygen of **5** although this does not lead to the most stable product, in agreement with experiment. Single-point energy calculations at higher levels do not change the qualitative conclusions.

Ketene (**1**) and substituted ketenes are reactive species with adjacent carbons subject to nucleophilic attack at C_1 and electrophilic attack at C_2.[1] Addition reactions to **1** have been rationalized using the frontier molecular orbital theory.[1a,c] Thus electrophilic attack occurs from above the plane involving the highest (HOMO) occupied molecular orbital, whereas nucleophiles approach in the plane to attack the lowest (LUMO) unoccupied molecular orbital.



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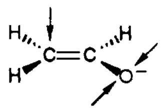

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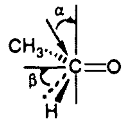

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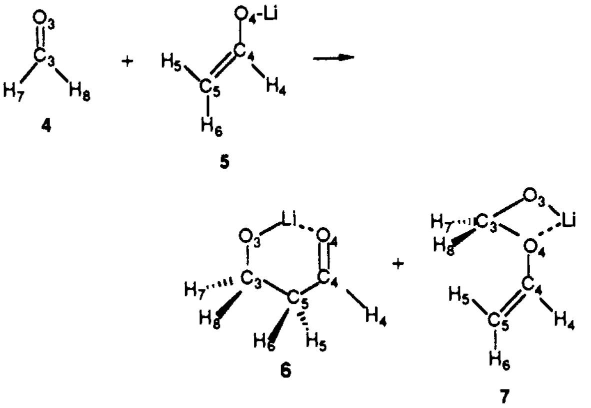
Enolates (**2**) are ambident nucleophiles[2] that can react with carbonyl compounds at either carbon or oxygen. For stereoelectronic reasons,[2f] attack of electrophiles at C occurs in the plane that is perpendicular to the plane of the enolate. However, approach to the oxygen occurs in the plane for maximum overlap (**2**).

The reactions of aldehydes and ketones with electrophiles have been of continuing experiment and theoretical interest, particularly regarding the stereochemistry of the reaction.[3,4] Recent theoretical studies have included additions of hydride,[3c,g-i] hydroxide,[3j] amines,[3k,l] and other nucleophiles.[3m] A study by Anh[3c] on the hydride addition to acetaldehyde has shown that the nucleophile approaches as shown in **3** in a nonvertical direction ($\alpha = 15.7°$) and from the side opposite the CH_3 group ($\beta = 18.3°$) consistent with the Dunitz–Burgi angle[3e] derived from crystallographic data.

In the prototypical reaction of formaldehyde (**4**) with the lithium enolate of acetaldehyde (**5**), reaction at either carbon or oxygen is possible leading to the aldol type product **6** or a hemi-acetal derivative **7**, respectively (eq 1). However, the former pathway invariably predominates.[4]



(1)

Ketenes behave differently in their reactions with enolates than do aldehydes and ketones.[5] Thus, we have recently shown that lithium enolates undergo acylation by ketenes to give O-acylated products (**8**, eq 2),[5c,d] contrary to the usual pattern of reaction at carbon of enolates by carbonyl compounds observed in the aldol condensation (**9**, eq 2).[4] Under some conditions the O-acylation by ketenes was reversible, and C-acylation was preferred at equilibrium.[5c,d]

In spite of the enormous effort devoted to study of the aldol reaction,[4] an ab initio theoretical study of the simple addition of lithium enolate of acetaldehyde (**5**) to formaldehyde (**4**) has only recently been reported.[6] The stereochemistry of the reaction involving enol borinates has been studied by a semiempirical

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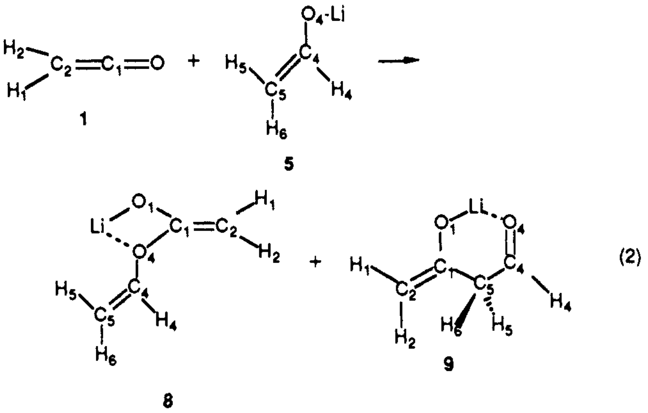


(2)

approach (MNDO).[7a] Ab initio results for C- and O-alkylation of acetaldehyde enolate with fluoromethane[2f,7b] as well as results on the addition of organolithiums[3h] or lithium hydride[3i] to formaldehyde (**4**) are available, and water addition to formaldehyde has been studied both experimentally[8a] and by an ab initio approach.[3m,8b]

This study was undertaken primarily to gain further insight into the thermodynamic reaction at carbon as compared to the kinetic O-acylation processes in the addition of $CH_2{=}CHOLi$ (**5**) to ketene (**1**) and to compare this to the reaction of formaldehyde (**4**) with **5** using the ab initio approach. While this study was underway, a study of C–C bond formation between **4** and **5** at the 3-21G basis set level was reported by Houk and coworkers.[6] Results obtained here are consistent with those reported.[6] Other recent reports relevant to this study are experimental thermochemical studies of an aldol reaction[9a] and theoretical studies of lithiated enamines,[9b] amide-coordinated organolithiums,[9c] and the reactions of lithium hydride or methyllithium with carbon dioxide,[9d] acrolein,[9e] and ketenes.[9f]

Computational Methods

Ab initio LCAO-MO-SCF calculations were performed using the program MONSTERGAUSS[10] in conjunction with either a GOULD 32/9705, a SUN 3260, or an APOLLO DN10000 minicomputer. The GAUSSIAN 86[11] package implemented with the CRAY X-MP/24 was also used.

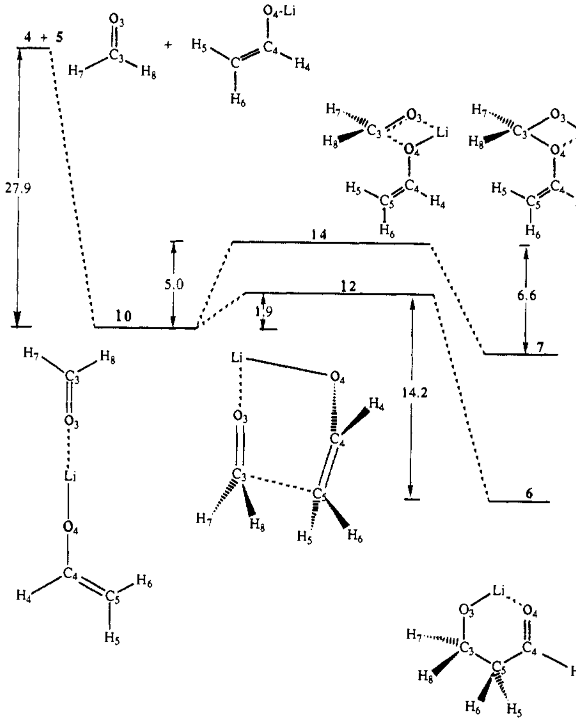
The geometries of the singlet ground state for all the molecules were fully optimized at the restricted Hartree–Fock level[12] using the standard 3-21G basis set by the optimally conditioned (OC)[12] method, except for the transition structures,[13] which required the use of the VA05[12] method.

The order of the critical points was determined by finite differences for every molecule computed at the 3-21G basis level. The order checks were performed by evaluating the second derivatives of the Hessian matrix by small changes in the optimized dihedral angles, bond lengths, and bond angles that would break any symmetry elements possessed by the molecules. Transition structures were characterized by establishing that the Hessian matrix had one and only one negative eigenvalue. The gradient optimizations were terminated when the gradient length was reduced to below 0.0005 mdyn.

Table I. Computed Energies for the Reaction of **5** with **1** and **4** (3-21G//3-21G)

structure	total energies, hartrees	dipole moment, D	critical order
1	150.87652	1.82	0
4	113.22182	2.66	0
5	158.92118	6.10	0
6	272.20699	3.53	0
7	272.18999	4.21	0
8	309.84188	5.13	0
9	309.86453	4.69	0
10a	272.18867	9.23	
10b	272.18750	11.03	0
10c	272.18749	10.89	
11	309.83336	1.05	
12	272.18441	2.62	1
13	309.82265	3.01	1
14	272.17945	3.39	1
15	309.82468	2.61	1

Scheme I. Energy Profile for the Addition of **4** to **5** (3-21G//3-21G, kcal/mol)



Results and Discussion

As in other recent theoretical studies of organolithium chemistry,[2f,6,9b,c,e] we have used the 3-21G basis set as the best compromise between the desire for accuracy in the results and the limitations of obtaining the results in a timely and cost effective manner. As has been pointed out by Houk and co-workers,[9b] geometries optimized for neutral species are expected to be reasonably reliable at the 3-21G level, and calculated *relative* energies are not expected to change with higher level calculations. We have, however, performed single-point energy calculations utilizing basis sets with both diffuse and polarization functions (6-31+G, 6-31G*, 6-31+G*)[12] for the HF/3-21G geometries at the HF level of theory to largely eliminate basis set superposition errors (BSSE).[9d,14] In addition, electron correlation energies were

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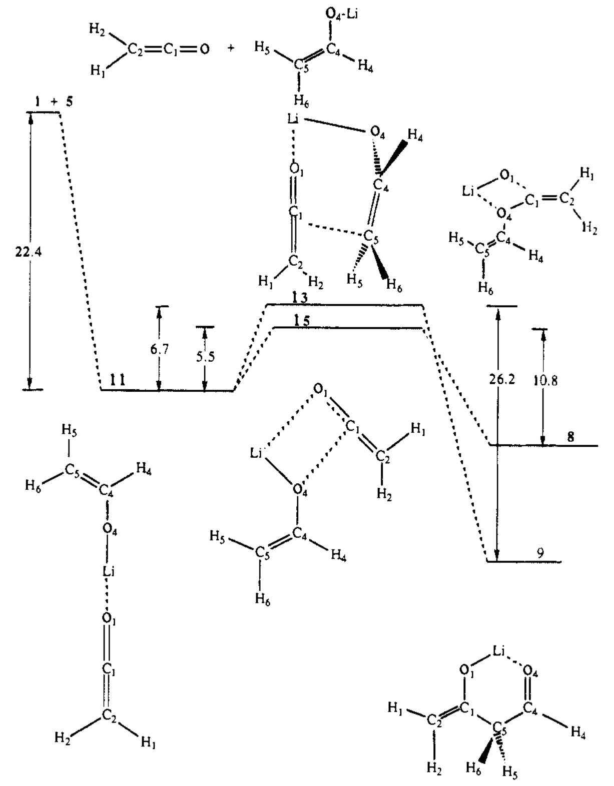
(12) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986.

(13) The transition state along the reaction coordination (Δ) is estimated from the ratio of the difference between the C–O bond lengths of the aldehyde (or ketene) moiety in the complex (A), the transition structures (B), and the products (C) Δ = (A − B)/(A − C) × 100).[3i]

(14) (a) Bachrach, S. M.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 2283–2287. (b) Kolos, W. *Theor. Chim. Acta* **1979**, *51*, 219–240.

Scheme II. Energy Profile for the Addition of **1** to **5** (3-21G//3-21G, kcal/mol)



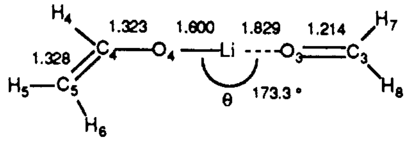
obtained at the Moller–Plesset level of theory (MP2/6-31+-G*//3-21G and MPi/6-31G*, i = 2–4).[12] As noted below, single-point energy calculations at higher levels using the 3-21G-optimized geometries did not affect the conclusions.

The 3-21G total energies, dipole moments, and critical order of all computed structures are given in Table I, and the single-point energy calculations are compared in Tables II and III. Calculated bond distances and angles are given in full in Tables IV and V. Total energies (hartrees) of **1** and **5–15** at different levels are given in Table VI. The relative energies (3-21G) are listed in Schemes I and II.

These studies were undertaken for the purpose of understanding our experimental work[5c,d] and as described below give surprisingly good agreement with both our results[5c,d] and those of others.[9a] It must be emphasized, however, that our computational model suffers from many limitations, including the basis set used, the absence of solvent, and the exclusion from consideration of lithium aggregates.[16] Since relative effects on somewhat similar reactions are compared, the latter two effects may not cause major problems, but caution must be exercised in interpreting small energy differences.

The essential features of the reaction mechanism for the reaction of **5** with **1** and with **4** have been investigated by examining the regions corresponding to (a) the separate reactants, (b) the complexes, (c) the transition structures, and (d) the products (Schemes I and II).

(A) Coordination Complexes. (i) CH_2=CHOLi (5) + CH_2=O (4). The first step of the reaction is formation of a complex **10** by dipole interaction between the oxygen and lithium atoms. The preferred approach of the oxygen of **4** toward the lithium atom of **5** was searched by varying the angle $\theta(O_3\text{–Li–}O_4)$ and the dihedral angle $\alpha(\text{Li–}O_3\text{–}C_3\text{–}H_8)$. Three stable complexes (**10a–c**) have been located and they are very similar in energy and in geometry, and although **10a** is more stable than **10b** and **10c** by 0.7 kcal/mol, this energy difference is too small to be of significance. This kind of complexation by lithium cation is well-known.[3h,i,6,9b-f] The direct observation of RLi-ketone complexes by IR spectroscopy was reported by Al-Aseer and Smith.[15]



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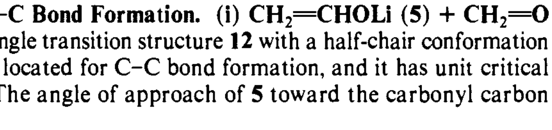
10	θ	α	relative energies, of 3-21G//3-21G, kcal/mol	DM, D
a	145.0	0.0	0.0	9.23
b	173.3	90.0	0.7	11.03
c	180.4	0.0	0.7	10.89

For further discussion, **10b** is chosen arbitrarily. This is a local minimum on the energy hypersurface. The electrostatic attraction lowers the total energies of the separate reactants by 27.9 kcal/mol (Scheme I).[6] The distance between Li and O_3 is 1.829 Å. The slight lengthening of the Li–O_4 and C_3–O_3 bond lengths (0.025 and 0.008 Å, respectively) is mainly due to the exothermicity of the reaction[3h] but indicates little change as compared to the separate reactants.

(ii) CH_2=CHOLi (5) + CH_2=C=O (1). Similarly to **10**, **1** and **5** associate in a linear fashion to form a stable complex **11** with a Li–O_1 bond length of 1.851 Å. The C_1–O_1 bond is lengthened by 0.011 Å and Li–O_4 by 0.020 Å. This electrostatic stabilization lowers the total energies by 22.4 kcal/mol (Scheme II), but this is 5.5 kcal/mol less than the stabilization gained on complexation of **4** and **5**. The 3-21G calculated charge density on oxygen is greater for CH_2=C=O (–0.54) than that for CH_2=O (–0.45) so this factor does not predict the greater stabilization gained on complexation of the latter. Other charge densities for CH_2=O are 0.130 (C) and 0.175 (H), while those for CH_2=C=O are +0.543 (C_1), –0.555 (C_2), and +0.279 (H).



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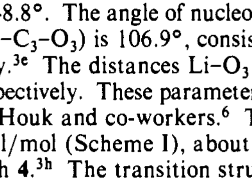
The stabilization energies due to the formation of the stable complexes are rather similar to those found for the addition of LiH to **4** (29.3 kcal/mol)[3h,i] and to **1** (23.5 kcal/mol) at the same level of calculation.[9f]

(B) C–C Bond Formation. (i) CH_2=CHOLi (5) + CH_2=O (4). A single transition structure **12** with a half-chair conformation has been located for C–C bond formation, and it has unit critical order. The angle of approach of **5** toward the carbonyl carbon (C_3–C_5–C_4) is 92.8°, with a dihedral angle C_3–C_5–C_4–O_4 of 68.5°, a C_3–C_5 distance of 2.370 Å, and a dihedral angle C_4–C_5–C_3–O_3 of 48.8°. The angle of nucleophilic attack on the carbonyl carbon (C_5–C_3–O_3) is 106.9°, consistent with the Dunitz–Burgi trajectory.[3e] The distances Li–O_3 and Li–O_4 are 1.765 and 1.718 Å, respectively. These parameters agree with those recently reported by Houk and co-workers.[6] The energy of activation is only 1.9 kcal/mol (Scheme I), about four times less than those for LiH with **4**.[3h] The transition structure is estimated[13] to be approximately 22% along the reaction coordinate.



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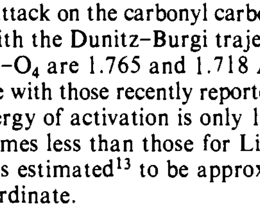

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(16) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1624–1654.

Table II. Relative Energies (kcal/mol) for the Reaction of **5** with **4**

	3-21G// 3-21G	6-31+G// 3-21G	6-31G*// 3-21	6-31+G*// 3-21G	MP2/ 6-31G*// 3-21G	MP3/ 6-31G*// 3-21G	MP4/ 6-31G*// 3-21G	MP2/ 6-31+G// 3-21G
4 + 5[a]	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10[a]	-27.9	-22.5	-19.4	-18.9	-19.0	-19.0	-19.3	-17.7
14[a]	-22.9	-17.3	-17.4	-16.0	-17.6	-17.3	-18.1	-16.1
7[a]	-29.5	-16.0	-17.0	-13.8	-22.1			-19.3
E_a(**14**–**10**)[b]	+5.0	+6.2	+2.0	+2.9	+1.4	+1.7	+1.2	+1.6
12[a]	-26.0	-15.0	-18.7	-15.7	-25.6	-22.6	-25.7	-22.6
6[a]	-40.2	-30.1	-35.7	-31.9	-40.3			-36.5
E_a(**12**–**10**)[c]	+1.9	+7.5	+0.7	+3.2	-6.6	-3.6	-6.4	-4.9
E(**7**–**10**)[d]	-1.6	+6.5	+2.4	+5.1	-3.1			-1.6
E(**6**–**10**)[e]	-12.3	-7.6	-16.3	-13.0	-21.3			-18.8
E(**14**–**12**)[f]	+3.1	-2.3	+1.3	-0.3	+8.0	+5.3	+7.6	+6.5
E(**6**–**7**)[g]	-10.7	-14.1	-18.7	-18.1	-18.2			-17.2

[a] Energy difference relative to separate reactants (**4**, **5**). [b] Activation energy for O–C bond formation. [c] Activation energy for C–C bond formation. [d] Exothermicity of O–C bond formation relative to **10**. [e] Exothermicity of C–C bond formation relative to **10**. [f] Energy difference between O and C transition state structures. [g] Energy difference between C–C and O–C products.

Table III. Relative Energies (kcal/mol) for the Reaction of **5** with **1**

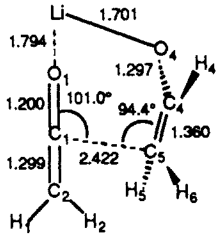
	3-21G// 3-21G	6-31+G// 3-21G	6-31G*// 3-21	6-31+G*// 3-21G
1 + 5	0.0	0.0	0.0	0.0
11[a]	-22.4	-17.6	-13.4	-13.2
15[a]	-16.9	-10.5	-8.8	-6.9
8[a]	-27.7	-19.4	-19.2	-16.4
E_a(**15**–**11**)[b]	+5.5	+7.1	+4.6	+6.3
13[a]	-15.7	-7.5	-9.6	-6.9
9[a]	-41.9	-38.9	-41.9	-39.3
E_a(**13**–**11**)[c]	+6.7	+10.1	+3.8	+6.3
E(**8**–**11**)[d]	-5.3	-1.8	-5.8	-3.2
E(**9**–**11**)[e]	-19.5	-21.3	-28.5	-26.1
E(**15**–**13**)[f]	-1.2	-3.0	+0.8	0.0
E(**9**–**8**)[g]	-14.2	-19.5	-22.7	-22.9

[a] Energy difference relative to separate reactants (**1**, **5**). [b] Activation energy for O–C bond formation. [c] Activation energy for C–C bond formation. [d] Exothermicity of O–C bond formation relative to **11**. [e] Exothermicity of C–C bond formation relative to **11**. [f] Energy difference between O and C transition-state structures. [g] Energy difference between C–C and O–C products.

The transition structure **12** then collapses to the product **6**, locked in a half-chair conformation primarily through the formation of the C_3–C_5 bond and with the lithium atom coordinating the two oxygens. The overall exothermicity of this reaction is 40.2 kcal/mol.

For comparison, the experimentally determined[9a] heat of reaction for the addition of lithium pinacolate (t-BuC(OLi)=CH$_2$) to pivaldehyde (t-BuCHO) in hexane at 25 °C is -30.2 kcal/mol. This experimental system differs from that studied theoretically in this work, but the high exothermicity found in both cases indicates qualitative agreement and argues against indications discussed elsewhere[9a] that aldol reactions may be near thermal neutrality. Major differences between the two systems include the use of pivaldehyde in the experimental study, and this substrate presumably has greater ground-state stabilization than formaldehyde; hence, a lower exothermicity is expected in the experimental reaction, as observed. Differential solvent effects between the reactants and products are evidently small, and this is plausible for the nonpolar hexane in which the lithium coordination to oxygen appears to dominate in both the solution phase studied experimentally and the gas phase studied theoretically.

(ii) CH_2=CHOLi (5) + CH_2=C=O (1). Similarly, a single transition structure **13** with a half-chair conformation was located, and it has unit critical order. This structure is remarkably similar to **12** for C-acylation of **4**. Thus the angle of approach of **5** toward the carbonyl carbon C_1–C_5–C_4 is 94.4°, with a dihedral angle C_1–C_5–C_4–O_4 of 68.5°, a C_1–C_5 distance of 2.422 Å, and a dihedral angle C_4–C_5–C_1–O_1 of 48.4°. The angle of nucleophilic attack (C_5–C_1–O_1) on the carbonyl compound corresponding to the Dunitz–Burgi trajectory is 101.0°, almost 6° less than the



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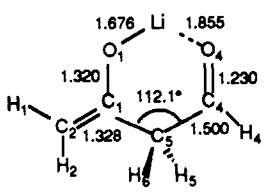

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Table IV. Calculated Bond Distances (Å) (3-21G)

bond	**1**	**4**	**5**	**6**	**7**	**8**	**9**	**10a**	**10b**	**10c**	**11**	**12**	**13**	**14**	**15**
C_1–C_2	1.2960					1.3214	1.3282				1.2858		1.2989		1.2937
C_1–C_5							1.5504						2.4221		
C_3–C_5				1.5905								2.3701			
C_4–C_5			1.3250	1.4910	1.3159	1.3124	1.5001	1.3272	1.3281	1.3280	1.3273	1.3636	1.3601	1.3277	1.3234
C_1–O_1	1.1620					1.2874	1.3203				1.1734		1.2003		1.1974
C_1–O_4						1.4924									2.1265
C_3–O_3		1.2069		1.3857	1.3457			1.2171	1.2139	1.2138		1.2510		1.2277	
C_3–O_4					1.5673									2.5851	
C_4–O_4			1.3305	1.2312	1.3705	1.3775	1.2299	1.3253	1.3233	1.3233	1.3247	1.2924	1.2970	1.3278	1.3390
C_2–H_1	1.0695					1.0684	1.0714				1.0708		1.0743		1.0709
C_2–H_2	1.0695					1.0655	1.0710				1.0709		1.0617		1.0633
C_3–H_7		1.0832		1.0888	1.0842			1.0789	1.0789	1.0789		1.0749		1.0767	
C_3–H_8		1.0832		1.0936	1.0842			1.0778	1.0789	1.0789		1.0756		1.0767	
C_4–H_4			1.0831	1.0831	1.0728	1.0677	1.0825	1.0854	1.0854	1.0856	1.0852	1.0849	1.0837	1.0837	1.0812
C_5–H_5			1.0736	1.0860	1.0721	1.0723	1.0904	1.0739	1.0741	1.0720	1.0739	1.0748	1.0754	1.0745	1.0741
C_5–H_6			1.0716	1.0812	1.0705	1.0701	1.0782	1.0719	1.0719	1.0740	1.0719	1.0730	1.0718	1.0712	1.0711
O_1–Li						1.7445	1.6762				1.8515		1.7942		1.8558
O_3–Li				1.6591	1.7202			1.8519	1.8290	1.8298		1.7650		1.8642	
O_4–Li			1.5740	1.8010	1.8300	1.8470	1.8550	1.5991	1.5999	1.5993	1.5944	1.7178	1.7010	1.6373	1.6894

Table V. Calculated Bond Angles (3-21G)

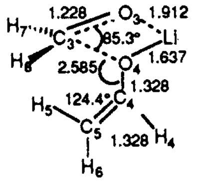
bond angle	**1**	**4**	**5**	**6**	**7**	**8**	**9**	**10a**	**10b**	**10c**	**11**	**12**	**13**	**14**	**15**
C_1-C_2-H_1	120.05					117.80	120.07				120.08		117.33		118.35
C_1-C_2-H_2	120.05					124.16	122.00				120.03		122.81		121.41
C_1-O_1-Li						95.38	125.83				175.04		136.17		102.63
C_1-O_4-C_4						126.34									132.22
C_1-C_5-C_4							112.11						94.39		
C_1-C_5-H_5							106.80								
C_1-C_5-H_6							112.16								
C_2-C_1-O_1						135.37	128.23				179.90		159.39		164.77
C_2-C_1-O_4						120.15									103.71
C_2-C_1-C_5							118.10						99.65		
C_3-C_5-C_4				111.23								92.76			
C_3-C_5-H_5				105.90											
C_3-C_5-H_6				111.55											
C_3-O_3-Li				124.54	93.48			134.97	175.92	179.24					
C_3-O_4-C_4					122.14									124.41	
C_4-C_5-H_5			121.44		123.40	122.12		121.40	121.36	120.79	121.40	119.45	120.06	121.77	121.85
C_4-C_5-H_6			120.75		119.56	120.28		120.75	120.80	121.37	120.76	119.68	119.56	120.88	120.67
C_4-O_4-Li			182.60					175.51	175.47	177.61	182.17	122.29		168.65	
C_5-C_3-O_3				111.40								106.73			
C_5-C_4-H_4			117.72	117.49	121.21	122.45	116.84	117.03	116.97	116.98	117.11	116.71	116.97	117.07	117.82
C_5-C_4-O_4			127.00	124.38	126.99	122.32	124.99	127.57	127.54	127.54	127.47	126.36	126.22	127.13	127.23
O_1-Li-O_4											167.41				
O_3-C_3-H_7		122.53		113.72				121.78	121.67	121.67		121.37		121.91	
O_3-C_3-H_8		122.53		113.49				121.24	121.67	121.66		121.35		121.91	
O_3-C_3-O_4					103.63									85.28	
O_3-Li-O_4								145.14	173.26	180.44					
O_4-C_3-H_7					103.54										
O_4-C_3-H_8					103.54										

corresponding angle in **12**. This restriction may arise in order to reduce repulsion between C_2 and C_5 in **13** and disappears in the products, where C_5–C_1–O_1 in **9** is 113.7°, compared to C_5–C_3–O_3 of 111.4° in **6**. The Li–O_1 and Li–O_4 distances are 1.794 and 1.701 Å, respectively. The energy of activation is 6.7 kcal/mol, and the transition state is estimated[13] to be around 19% along the reaction coordinate.

The transition structure **13** collapses to the C-acylated product **9** primarily through the formation of the C_1–C_5 bond, with the lithium atom coordinating the two oxygens in a half-chair conformation. The overall exothermicity of the reaction is 41.9 kcal/mol.

For comparison, the activation energies for reactions of LiH and CH_6Li with CH_2=O[3h] and CH_2=C=O[9f] are rather similar to those described here, although the former reactions are all at least 30 kcal/mol more exothermic. These reactions will be discussed in full in a future publication.[9f]

(C) O–C Bond Formation. (i) CH_2=CHOLi (5) + CH_2=O (4). A planar four-centered transition structure **14**, characterized by a single imaginary frequency, for O–C bond formation has been located. The angle of attack (O_3–C_3–O_4) on the carbonyl is 85°



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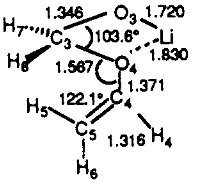

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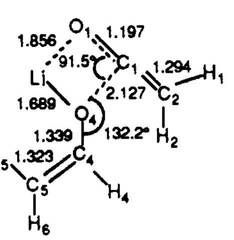
with a C_3–O_4 distance of 2.585 Å. This attack angle is greatly restricted compared to that for C-acylation in **12** of 107° due to the coordination of the lithium to both oxygens in **14**. There is little change in the structural parameters as compared to those of the complex **10b** or the separate reactants (**4** and **5**), suggesting an early transition state estimated[13] to be 10% along the reaction coordinate. The distances Li–O_3 and Li–O_4 are 1.912 and 1.637 Å, respectively. The energy of activation for formation of **14** is 5.0 kcal/mol, three times higher than that for C–C bond formation, which explains the normal absence of this pathway in the aldol reaction.

In the next step, **14** collapses to the product **7** primarily through the formation of the C_3–O_4 bond. The product **7** is planar, four-centered with the Li atom bridging the two atoms. The C_3–O_4 bond length for **7** is unusually long (1.567 Å), and the parameters for the enolate moiety are not very different from those found for **5**, **10b**, or **14**.

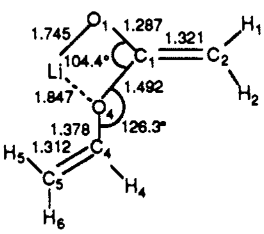
Product **7** is more stable than the complex **10b** by only 1.6 kcal/mol, whereas the C–C bonded product **6** is more stable than **10b** by 12.3 kcal/mol. The overall exothermicity for the formation of **7** is 29.5 kcal/mol compared to 40.2 for C–C bond formation and 71.5 for LiH with **4**.[3h]

For comparison, the angle of attack of water on **4** was found to be 88.3° with an overall exothermicity of 16.7 kcal/mol forming a methanediol product with a C–O bond length of 1.411 Å (4-31G).[3m,8b] The C(sp^2)–O and C(sp^3)–O bond lengths for methyl vinyl ether[2f] at the 3-21G level are 1.370 and 1.437 Å, respectively.

(ii) CH_2=CHOLi (5) + CH_2=C=O (1). O-Acylation occurs via a planar, four-centered transition structure **15**. The angle of attack on the carbonyl (O_1–C_1–O_4) is 91.5°, and C_1–O_4 is 2.127 Å. The corresponding attack angle for C-acylation in **13** was



15



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101°, and the restriction in the angle in **15** is caused by the coordination of both oxygens to lithium, as already noted for **14**. Interestingly, the attack angle on ketene for both C-acylation (in **13**) and O-acylation (in **15**) is significantly nearer to 90° than for the corresponding attack on formaldehyde (in **12** and **14**). For **13** this was suggested above to possibly involve a steric effect, but this would not apply for **15** and there may be an electronic reason involving attack on this sp-hybridized carbon in **1** as well. In any event the structural changes in **15** compared to the reactants are small, suggesting an early transition state estimated[13] to be 13% along the reaction coordinate.

The activation energy for formation of **15** is 5.5 kcal/mol, comparable to that found for LiH with **1**. However, it is 1.2

Table VI. Computed Energies for the Reaction of **5** with **1** and **4**

	total energies, hartrees							
species[a]	3-21G//3-21G	6-31+G//3-21G	6-31G*//3-21	6-31+G*//3-21G	MP2/6-31G*//3-21G	MP_3/6-31G*//3-21G	MP4/6-31G*//3-21G	MP2/6-31+G*//3-21G
1 (0)	150.876 52	151.654 16	151.723 94	151.729 07				
4 (0)	113.221 82	113.812 51	113.865 29	113.870 19	114.116 81	114.172 49	114.190 70	114.176 00
5 (0)	158.921 18	159.757 51	159.795 10	159.805 69	160.238 55	160.249 93	160.275 39	160.253 74
6 (0)	272.206 99	273.618 04	273.717 25	273.726 70	274.469 57			274.487 92
7 (0)	272.189 99	273.595 51	273.687 41	273.697 90	274.440 52			274.460 48
8 (0)	309.841 88	311.442 66	311.549 70	311.560 82				
9 (0)	309.864 53	311.473 71	311.585 74	311.597 44				
10 (0)	272.187 50	273.605 92	273.691 37	273.706 05	274.435 58	274.452 78	274.496 83	274.457 92
11 (0)	309.833 36	311.439 76	311.540 42	311.555 81				
12 (1)	272.184 41	273.593 94	273.690 21	273.700 82	274.446 08	274.458 50	274.507 11	274.465 83
13 (1)	309.822 65	311.423 68	311.534 26	311.545 71				
14 (1)	272.179 45	273.597 65	273.688 05	273.701 34	274.433 40	274.449 97	274.494 94	274.455 45
15 (1)	309.824 68	311.428 40	311.533 02	311.545 69				

[a] The values given in parentheses are the number of negative eigenvalues in the Hessian matrix.

kcal/mol (Scheme II) lower in energy than that for C-acylation whereas O–C bond formation for **4** and **5** is higher in energy by 3.1 kcal/mol compared to C–C bonding.

In the next step, **15** collapses to the O-acylated product **8** through the formation of the C_1–O_4 bond. The product **8** is a minimum on the energy hypersurface.

It is planar, four-centered with the lithium atom bridging the two oxygen atoms. The C_4–O_4 and C_1–O_4 bond lengths are 1.378 and 1.492 Å, respectively, quite close to those found for methyl vinyl ether (1.370 and 1.437 Å).[2f] The overall exothermicity of the reaction is 27.7 kcal/mol, but this is 14.2 kcal/mol less favorable than for C-acylation. Experimentally[5c,d] we observed that enolates have a kinetic preference for O-acylation by ketenes but that C-acylation is favored at equilibrium, consistent with the calculations.

Interestingly, C–C bond formation between CH_2=O (**4**) and CH_2=CHOLi (**5**) is only 10.7 kcal/mol more favorable than for C–O bond formation, whereas for CH_2=C=O (**1**) and **5**, C–C bond formation is 14.2 kcal/mol more favorable. The origin of this difference is not clear. Conversion of the complex **10b** formed from **4** and **5** to the C–O bonded product **7** is exothermic by only 1.6 kcal/mol, whereas formation of the complex **11** from **1** and **5** is 5.5 kcal/mol less exothermic than formation of **10b**, and conversion of **11** to the C–O bonded product **8** is exothermic by 5.3 kcal/mol.

(D) Single-Point Energy Calculations. Single-point energy determinations including electron correlation at the MP4/6-31G*//3-21G[12] and MP2/6-31+G*//3-21G[12] levels of theory were performed for the 3-21G-optimized geometries and are summarized in Tables II and III as the energies relative to the reactant pairs **4** + **5** and **1** + **5** corresponding to the energy profiles of Schemes I and II. For both reactions the C–C bonded products are indicated to be even more stable than the O–C bonded products, while the effects on the relative transition-state energies for C–C and O–C bond formation are much smaller, so that the transition states for C–C and O–C bond formation are similar in both cases. The possibility of a kinetic preference for O–C bond formation even though C–C bond formation is highly favored thermodynamically is thus supported by the calculations at all levels.

In every case the linear structures **10b** and **11** remain as distinct energy minima with single-point energy calculations. The stabilization energy gained on complexation for both **10b** and **11** relative to their separate reactants, calculated at higher levels of theory (including electron correlation for **10b**) (Tables II and III), are all less negative by ca. 9 kcal/mol compared to the 3-21G results. It is well documented that the small 3-21G basis set does not allow sufficient functional flexibility for the description of Li–heteroatom interaction, thereby resulting in an artificial stabilization of the complexes by at least 9 kcal/mol due to basis set superposition error (BSSE).[9d,12] The association energy for CH_2=OLiH complexation (MP2/6-31+G*//6-31G*) including zero-point energy was calculated by Schleyer and his co-workers to be −16.1 kcal/mol.[9d]

The activation energies for both O–C and C–C bond formation are substantially dependent on the basis set and electron correlation.[9d,12] The activation energy for O–C bond formation including electron correlation is rather low, ca. 1.2–1.7 kcal/mol at the MP levels (Table II), whereas C–C bond formation is "barrierless" (−4 to −7 kcal/mol). Although these values are substantially different from the 3-21G results in absolute terms, they are consistent with the qualitative observations and conclusions reached earlier with the 3-21G basis set level in that C–C bond formation for the reaction of CH_2=O (**4**) and CH_2=CHOLi (**5**) is favored over O–C bond formation. Precedent for a negative activation energy was reported for the reaction of CO_2 and LiH[9d] (4.7 kcal/mol at 6-31+G*//6-31G* and −0.2 kcal/mol at MP2/6-31+G*//6-31G*).

The rather large negative activation energy for C–C bond formation is presumably due to the fact that the single-point calculations at the MP levels are carried out using HF/3-21G-optimized structures. A more accurate estimate would require the geometry optimizations to be performed at least at the HF/6-31G*, but computation of molecules such as **12** and **13** at this level is time consuming and is not economically feasible at the present time.

Conclusion

The lithium cation plays an important role in the reactions of CH_2=CHOLi (**5**) with CH_2=O (**4**) and CH_2=C=O (**1**) by coordinating with the two oxygens in the complexes, the transition structures, and the products. In the reaction of **4** at the oxygen of **5** a weak C–O bond is formed, whereas reaction at carbon involves formation of a strong C–C bond. The 40.2 kcal/mol exothermicity of this latter process is consistent with the 30.2 kcal/mol exothermicity found experimentally for a related process in solution.[9a] Reaction of CH_2=O at the oxygen of CH_2=CHOLi involves interconversion of a complex and product of the same order of stability with a relatively low activation energy, whereas attack at carbon has a higher exothermicity with a lower activation energy. The activation energy for O-acylation by ketene is 1.2 kcal/mol lower as compared to that for C-acylation of **5** by **1**. However, the C-acylated product **9** is more stable than the O-acylated product **8** by 14.2 kcal/mol. This is in agreement with the experimental observation in solution that whereas ketenes give a kinetic preference for O-acylation of enolates, C-acylation is favored at equilibrium.[5c,d].

As already noted, these computations suffer from basis set limitations and do not consider the effect of solvent and aggregation of the lithium species. While it may be fortuitous that the calculations do agree with the experimental observation of preferred kinetic O-acylation despite the strong thermodynamic preference for C-acylation, some confidence can be placed in the fact that the calculations correctly predict that kinetically O-acylation and C-acylation are competitive, whereas there is a strong preference for the latter at equilibrium.

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Series of Two-Coordinate and Quasi-Two-Coordinate Transition-Metal Complexes: Synthesis, Structural, and Spectroscopic Studies of Sterically Demanding Borylamide Ligands $-NRBR'_2$ (R = Ph, R' = Mes, Xyl; R = R' = Mes), Their Lithium Salts $Li(Et_2O)_2NRBR'_2$, and Their Transition-Metal Derivatives $M(NPhBMes_2)_2$ (M = Cr, Co, Ni), $Co(NPhBXyl_2)_2$, and $M(NMesBMes_2)_2$ (M = Cr → Ni)

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Abstract: Amide ligands, modified by the presence of the diarylboryl substituents $-BMes_2$ or $-BXyl_2$ (Mes = 2,4,6-$Me_3C_6H_2$, Xyl = 2,6-$Me_2C_6H_3$), have been used to effect the synthesis and characterization of several low-coordinate metal complexes of unusual structure. The synthesis of the aminoboranes $HNRBMes_2$ (R = Ph, **1**; R = Mes, **2**) and $HNPhBXyl_2$ (**1a**), the lithium borylamide salts $Li(Et_2O)_2NRBMes_2$ (R = Ph, **3**; R = Mes, **4**), and 10 transition-metal derivatives, $M(NPhBMes_2)_2$ (M = Cr, **5**; Co, **6**; Ni, **7**), $Co(NPhBXyl_2)_2$ (**6a**), $Co[N(C_6D_5)BMes_2]_2$ (**6b**), and $M(NMesBMes_2)_2$ (M = Cr, **8**; Mn, **9**; Fe, **10**; Co, **11**; Ni, **12**), are reported. The X-ray crystal structures of **2**, **4–7**, **10**, and **11** are described and discussed in the context of structures **1**, **3**, **8**, **9**, and **12** reported in preliminary publications. The transition-metal complexes were further characterized by UV/vis and EPR spectroscopy and magnetic data. Variable-temperature ^1H NMR spectroscopy of **6**, **6a**, **6b**, **7**, **11**, and **12** is also reported. The transition-metal complexes **5–12** are all high spin with nominally two-coordinate geometries. However, they all display some deviation from linearity. The distortion is most severe for the chromium complexes **5** and **8** (N–Cr–N = 110.8 (1)° and 112.3 (3)°) whereas in Fe, Co, and Ni derivatives of $-NMesBMes_2$ deviation of the NMN angle from 180° is only about 13°. The BN bonds within the ligands are short, and the nitrogen and boron centers are invariably planar. The ligands are, in effect, boron–nitrogen analogues of alkenyls. Instead of association through bridging at the nitrogen centers, moderate (in **5–8**) or very weak (in **9–12**) intramolecular interactions are observed between the ipso carbons of the $-BMes_2$ groups and the metal centers that may cause the observed structural distortions. Variable-temperature ^1H NMR data on **6**, **6a**, **6b**, and **11** indicate that the M···C ligand interactions are not greater than about 10 kcal mol^{-1} for **6**, **6a**, **6b**, and presumably for **5** and **7**, whereas in the NMes compounds **11** and **12** no M–C interactions could be detected at temperatures as low as 192 K. Crystal data with Mo Kα (λ = 0.71069 Å) radiation at 130 K: **2**, $HNMesBMes_2$, $C_{27}H_{34}BN$, a = 8.200 (1) Å, b = 10.370 (3) Å, c = 15.134 (3) Å, α = 109.38 (2)°, β = 80.96 (2)°, γ = 108.71 (2)°, Z = 2, triclinic, space group $P\bar{1}$, R = 0.063; **4**, $Li(Et_2O)_2NMesBMes_2$, a = 10.927 (4) Å, b = 19.626 (5) Å, c = 31.07 (1) Å, Z = 8, orthorhombic, space group *Pbca*, R = 0.085; **5**, $Cr(NPhBMes_2)_2$, $C_{48}H_{54}B_2CrN_2$, a = 11.344 (2) Å, b = 22.531 (8) Å, c = 16.285 (3) Å, β = 94.95 (1)°, Z = 4, monoclinic, space group $P2_1/c$, R = 0.046; **6**, $Co(NPhBMes_2)_2$, $C_{48}H_{54}B_2CoN_2$, a = 13.454 (3) Å, b = 15.466 (4) Å, c = 23.191 (7) Å, β = 99.82 (2)°, Z = 4, monoclinic, space group $P2_1/n$, R = 0.080; **7**, $Ni(NPhBMes_2)_2$, $C_{48}H_{54}B_2NiN_2$, a = 10.616 (4) Å, b = 12.108 (4) Å, c = 17.578 (4) Å, α = 109.27 (2)°, β = 91.89 (3)°, γ = 103.05 (3)°, Z = 2, triclinic, space group $P\bar{1}$, R = 0.057; **10**, $Fe(NMesBMes_2)_2$, $C_{56}H_{66}B_2FeN_2$, a = 11.462 (5) Å, b = 13.784 (6) Å, c = 15.797 (6) Å, α = 103.35 (3)°, β = 101.51 (3)°, γ = 99.87 (4)°, Z = 2, triclinic, space group $P\bar{1}$, R = 0.045; **11**, $Co(NMesBMes_2)_2$, $C_{54}H_{66}B_2CoN_2$, a = 11.399 (5) Å, b = 13.746 (7) Å, c = 15.852 (7) Å, α = 103.13 (4)°, β = 101.76 (4)°, γ = 99.71 (4)°, Z = 2, triclinic, space group $P\bar{1}$, R = 0.057.

Recent results from a number of laboratories have shown that it is possible to achieve a two-coordinate geometry in some open-shell (d^0–d^9) transition-metal complexes under ambient conditions.[1-8] Hitherto this coordination number had been restricted to transition-metal dihalides at high temperature in the gas phase[9] or to species with a closed-shell (d^{10}) electron configuration, for example, complexes of Pt(0), Cu(I), Ag(I), or Hg(II). However, two early papers[10,11] suggested that the divalent

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