

# Molecular Structure of the Lithium Enolate of Acetaldehyde

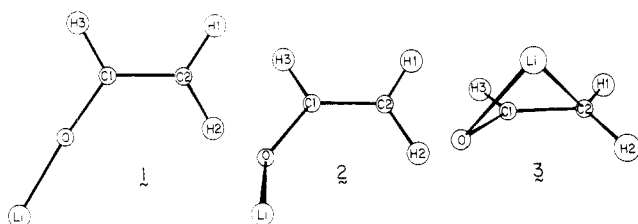
Thomas J. Lynch, Martin Newcomb,\* David E. Bergbreiter,\* and Michael B. Hall\*

Department of Chemistry, Texas A&M University,  
College Station, Texas 77843

Received May 22, 1980

Lithio anions stabilized by carbonyl or related groups are ubiquitous in synthetic organic chemistry as a form of nucleophilic carbon. However, in spite of their importance, surprisingly little is known of the structure and in particular of the topology of these compounds.<sup>1,2</sup> As an outgrowth of other interests in electrophilic asymmetric synthesis, we have undertaken theoretical calculations aimed at discerning the range of topological isomers which could reasonably be expected for lithium enolates. The results suggest that the "gas-phase" lithium enolate of acetaldehyde would be chiral with a structure similar to that of a delocalized allyllithium, although a planar structure with the lithium bound to oxygen is close in energy.

The calculations were done at the restricted Hartree-Fock level<sup>3</sup> with the HONDO program<sup>4</sup> on the CDC 7600 at Lawrence Berkeley Laboratory. In the first set of calculations, the standard 4-31G basis set<sup>5</sup> (5-21G on lithium)<sup>6</sup> was used and the program was allowed to optimize fully the geometry. The three lowest energy structures are 1-3.



Structures 1 and 3, which appear to be local minima, were converged until the largest term in the gradient was below 0.0003 au/au and the change in the total energy per gradient cycle was less than 0.000001 au. Structure 2, which has a gradient below 0.004, represents an undefined point of low gradient on the hypersurface connecting structures 1 and 3, and it is included because it illustrates the extremely flat nature of this potential-energy surface. Structure 1 is a planar lithium enolate with a C-O-Li bond angle of 175.6°, an angle close to that of other R-O-Li systems.<sup>7</sup> Structure 2 corresponds to a nearly planar enolate with the lithium rotated out of the plane 48°. Structure 3 is a nonplanar enolate with the lithium bound to the oxygen, but interacting strongly with the  $\pi$  system of the carbon-carbon double bond. The latter structure resembles that of a delocalized allyllithium, which is the most stable geometry for other organolithium salts.<sup>8</sup> The

Table I. Optimized Geometries, Total Energies, and Relative Energies for Structures 1-3

	1	2	3
bond lengths, Å			
H(1)-C(2)	1.071	1.070	1.070
H(2)-C(2)	1.073	1.077	1.080
H(3)-C(1)	1.080	1.079	1.079
C(1)-C(2)	1.326	1.330	1.353
C(1)-O	1.328	1.331	1.319
O-Li	1.608	1.652	1.749
bond angles, deg			
H(1)-C(2)-C(1)	121.0	121.3	121.5
H(2)-C(2)-C(1)	121.4	121.0	120.7
H(3)-C(1)-C(2)	118.7	119.7	119.4
C(2)-C(1)-O	126.4	125.4	123.6
C(1)-O-Li	175.6	130.5	90.1
dihedral angles, deg			
H(1)-C(2)-C(1)-O	180.0	176.2	174.2
H(2)-C(2)-C(1)-O	0.0	-6.7	-20.0
H(3)-C(1)-C(2)-O	180.0	178.4	174.2
C(2)-C(1)-O-Li	0.0	48.2	42.9
total energies, au			
4-31G(5-21G Li)	-159.58855	-159.58070	-159.57744
[3s2p1d/3s2p/2s]	-159.65343	-159.64983	-159.65572
relative energies, kcal mol <sup>-1</sup>			
4-31G(5-21G Li)	0.00	2.24	6.97
[3s2p1d/3s2p/2s]	1.44	3.84	0.00

optimized geometries and energies are given in Table I. It is well-known that the 4-31G basis produces excessively large bond angles, especially at atoms with lone-pair electrons.<sup>5</sup> Thus, it is not surprising that this basis set favors structure 1, the most open of the three structures. Addition of polarization functions, particularly  $d$  functions, on the heavy atoms, usually corrects this situation. Particularly relevant to this study are recent theoretical calculations on the structure of ammonia and formamide in various basis sets,<sup>11</sup> where it was shown that the 4-31G basis yielded inferior results, while a double  $\zeta$  plus polarization basis yielded results in close agreement with experiment. Therefore, we have recalculated the total energies of these three structures using the recent Dunning and Hay [3s2p/2s] contraction (double  $\zeta$ ) augmented by polarization ( $d$ ) functions on the carbons and oxygen.<sup>12</sup> The results (Table I) show that the lowest energy structure is 3, a chiral lithium enolate with an allyllithium-like ge-

(1) Jackman, L. M.; Lange, B. C. *Tetrahedron* 1977, 33, 2737.

(2) Considerable work has been done on all carbon species, for example, see: Jemmis, E. D.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1979, 101, 2848.

(3) Roothaan, C. C. *J. Rev. Mod. Phys.* 1951, 23, 69.

(4) Dupuis, M.; Rys, J.; King, H. F. *J. Chem. Phys.* 1976, 65, 111. Dupuis, M.; King, H. F. *Ibid.* 1978, 68, 3998.

(5) Pople, J. A. In "Applications of Electronic Structure Theory"; Schaefer, H. F., Ed.; Plenum Press: New York, 1979; Chapter 1.

(6) Dill, J. D.; Pople, J. A. *J. Chem. Phys.* 1975, 62, 2921. We have used unscaled Li functions. Scaled Li functions reproduce our geometries to within 0.004 Å and 0.5° and our energy difference (3-1) to within 0.3 kcal/mol (Schleyer, P. v. R.; Clark, T., unpublished results).

(7) Dill, J. D.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A. *J. Am. Chem. Soc.* 1977, 99, 6159.

(8) There exists a regular decrease in the stability of the allyl-like geometry relative to that of the planar geometry as carbon-1 of allyllithium is replaced first by a nitrogen atom and then by an oxygen atom. Clark et al.<sup>9</sup> found that for allyllithium the  $\pi$ -bonded structure is 15.7 kcal/mol more stable than the planar structure, and Houk et al.<sup>10</sup> determined that in a lithium salt of an imine the  $\pi$ -bonded structure is 4.0 kcal/mol more stable than the planar structure.

(9) Clark, T.; Jemmis, E. D.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A. *J. Organomet. Chem.* 1978, 150, 1.

(10) Houk, K. N.; Strozler, R. W.; Rondan, N. G.; Fraser, R. R.; Chuaqui-Offermans, N. *J. Am. Chem. Soc.* 1980, 102, 1426. We thank Professor Houk for informing us of these results prior to publication.

(11) Carlsen, N. R.; Radom, L.; Riggs, N. V.; Rodwell, W. R. *J. Am. Chem. Soc.* 1979, 101, 2233.

(12) Dunning, T. H.; Hay P. J. In "Methods of Electronic Structure Theory"; Schaefer, H. F., Ed.; Plenum Press: New York, 1977; Chapter 1.

ometry. Structure 2 is now higher in energy than either 1 or 3. Although a complete geometry optimization in this larger basis was not feasible, two cycles of the gradient procedure increased the energy difference between structure 1 and 3 to 1.95 kcal/mol.

The energy differences between the various enolate structures are small and could be modified by solvent effects which are neglected in our calculations. In addition, simple enolates probably exist as aggregates which can vary in average size as a function of solvent or concentration.<sup>13</sup> Nevertheless, the conclusion that chiral enolates are low-energy structures is important as a guide for future study in asymmetric syntheses involving chiral nucleophiles. This conclusion suggests that enolates containing internal ligands may be prepared such that a new chiral center would exist by virtue of the counterion position. A recent structure of a substituted lithium phenoxide dimer provides an example of a potentially chiral  $\pi$ -stabilized lithium-oxygen species which has some structural similarities to the chiral species 2 we describe above.<sup>14</sup> Our proposal finds further precedent in some recent work by Posner in which an internal arene was postulated to act as a ligand

for an out-of-plane lithium in some cyclic enolates.<sup>15</sup> Topological arguments for out-of-plane lithium have also been at least implied in speculation about the basis of some successful asymmetric syntheses.<sup>16</sup> From the results of our calculations, we believe these are the very sort of lithium enolates likely to have an even stronger preference for an out-of-plane lithium than the acetaldehyde enolate and that further studies of lithio enolates may lead to unambiguous demonstration of a chiral lithium enolate.

**Acknowledgment.** This research was supported in part by the National Resource for Computation in Chemistry under a grant from the National Science Foundation and the Basic Energy Sciences Division of the United States Department of Energy under contract No. W-7405-ENG-48. Partial support of this work by the National Institutes of Health (Grant GM 26268) and donors of the Petroleum Research Fund, administered by the American Chemical Society, is also gratefully acknowledged. Dr. M. Dupuis of the NRCC is thanked for his help with the HONDO program. We thank Professor P. v. R. Schleyer for several helpful comments.

**Registry No.** Lithium acetaldehyde enolate, 2180-63-4.

(13) Jackman, L. M.; Szeverenyi, N. M. *J. Am. Chem. Soc.* **1977**, *99*, 4954.

(14) The structure of lithium 2,6-di-*tert*-butylphenoxide, which was recently reported, is achiral only by virtue of the high symmetry of the phenoxide ligands: Cetinkaya, B.; Gumrukcu, I.; Lappert, M. F.; Atwood, J. L.; Shakir, R. *J. Am. Chem. Soc.* **1980**, *102*, 2088.

(15) Posner, G. H.; Lentz, C. M. *J. Am. Chem. Soc.* **1979**, *101*, 934.

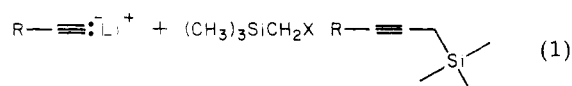
(16) Meyers, A. I.; Whitten, C. E. *Heterocycles* **1976**, *4*, 1687. Davenport, K. G.; Eichenauer, H.; Enders, D.; Newcomb, M.; Bergbreiter, D. E. *J. Am. Chem. Soc.* **1979**, *101*, 5654.

## Communications

### Preparation of a Terminal Allene, 3-Haloallene, and 3-Acyallene from a Propargyltrimethylsilane

**Summary:** Preparations of a terminal allene, 3-haloallene, and 3-acyallene from the reaction of a propargyltrimethylsilane with trifluoroacetic acid, bromine or iodine, and acetyl chloride-aluminum chloride, respectively, are reported.

**Sir:** Recently the previously little-studied propargyltrimethylsilanes have become readily accessible from the reaction of the lithium salts of alkynes with (trimethylsilyl)methyl halides<sup>1</sup> or triflate (trifluoromethanesulfonate)<sup>1,2</sup> (eq 1). In a reaction comparable to reactions



of allylsilanes,<sup>3</sup> a propargylsilane containing a tosylate initiator has recently been shown to undergo an intramolecular electrophilic cyclization to give a five-membered ring having an exocyclic allene group.<sup>2</sup> Importantly, a similar reaction has now been utilized in Johnson's laboratory to form ring D of a steroid precursor.<sup>4</sup>

On the contrary, propargyltrimethylsilane did not give a  $TiCl_4$ -catalyzed reaction with adamantyl chloride under conditions where allyltrimethylsilane gave the typical carbon-carbon bond formation with concomitant double bond shift.<sup>5</sup> Reactions of  $(CH_3)_3SiC\equiv CCH_2Si(CH_3)_3$  with electrophiles  $Br_2$ ,  $SO_3$ ,  $MeSO_3H$ , and  $ClSO_3SiMe_3$  did give some expected products of electrophilic attack with cleavage of Si.<sup>6a,b</sup> A comparable reaction of acetals was very recently reported.<sup>6c</sup>

We have explored the reactions of propargyltrimethylsilanes with several electrophiles and with  $NaOEt$  to give the results shown in Scheme I. Of particular interest in Scheme I is the reaction with the electrophile,  $H^+$ , which gave, after distillation, pure allene 2 in moderate yield. This reaction, in conjunction with our propargylsilane preparation, constitutes a convenient *two-step preparation of a terminal allene from the terminal alkyne having one fewer carbon atoms*. Presently, such allenes are preparable from the alkene having one fewer carbon atoms through reaction with dibromocarbene, followed by an alkyl-lithium,<sup>7a</sup> or from an aldehyde having two fewer carbon atoms by reaction with  $\alpha$ -silylvinyl carbanions followed by subsequent transformations.<sup>7b</sup>

(4) Schmid, R.; Huesman, P. L.; Johnson, W. S. *J. Am. Chem. Soc.* **1980**, *102*, 5122. We thank Professor Johnson for a preprint of this paper.

(5) Sasaki, T.; Usuki, A.; Ohno, M. *Tetrahedron Lett.* **1978**, 4925.

(6) (a) Bourgeois, P.; Merault, G. C. R. *Hebd. Seances Acad. Sci., Ser. D* **1971**, 273, 714. (b) Bourgeois, P.; Merault, G. *J. Organomet. Chem.* **1972**, *39*, C44. (c) Pornet, J. *Tetrahedron Lett.* **1980**, 2049.

(7) (a) Taylor, D. R. *Chem. Rev.* **1967**, *67*, 317. (b) Chan, T. H.; Mychajlowskij, W.; Ong, B. S.; Harp, D. N. *J. Org. Chem.* **1978**, *43*, 1526.

(1) Chiu, S. K.; Peterson, P. E. *Tetrahedron Lett.*, in press.  
(2) Despo, A. D.; Chiu, S. K.; Flood, T.; Peterson, P. E. *J. Am. Chem. Soc.* **1980**, *102*, 5121.

(3) Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761.