

(*E,E*)-enolate could be used to obtain the adduct in reasonable diastereomeric purity simply by adding less halide to the dianion.

In summary, the dianion strategy described herein illustrates a practical, flexible, and efficient enantioselective carbocyclization process. The scope and detailed mechanism of this reaction are under intense investigation and will be presented in due course.

X-ray Crystal Structure of an Unsolvated Lithium Enolate Anion

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A number of studies^{1,2} are devoted to establishing the structure and reactivity of lithium enolate anions because these species are very important reactive intermediates in synthetic organic chemistry. A few recent X-ray analyses³ have just begun to unravel the details of the solid-state structures of these and related species despite the fact that lithiated ester enolates were isolated as stable crystalline solids over 10 years ago.⁴ An X-ray diffraction analysis of the unsolvated lithium enolate of *tert*-butyl methyl ketone is now reported. This structure determination yields a completely novel structural type with useful stereochemical implications.

Clear, prismatic crystals of the lithium enolate of pinacolone were grown from hydrocarbon solvent at $-20\text{ }^{\circ}\text{C}$ following a procedure slightly modified from that reported.⁵ These crystals remain suitable for diffraction analysis if they are kept below $-5\text{ }^{\circ}\text{C}$. Upon warming to room temperature, the crystals become opaque within minutes and gradually crumble to a fine powder.⁶ X-ray diffraction data was collected in two shells utilizing two different crystals kept below $-100\text{ }^{\circ}\text{C}$ in a stream of dry nitrogen.⁷ A tangent refinement with random starting phases solved the crystal structure.⁸ The crystallographic asymmetric unit consists of two independent half-hexamers.⁹ Each of these units sits on

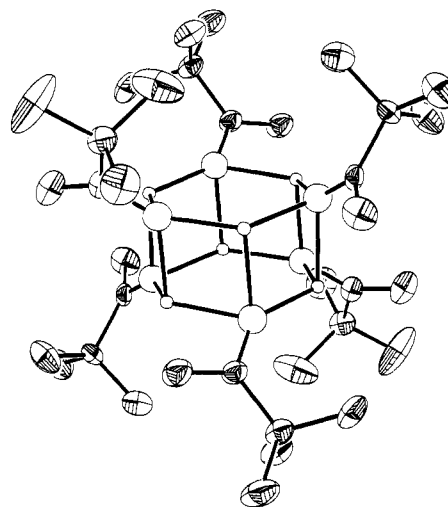


Figure 1. Hexameric pinacolone enolate; large circles = oxygen, small circles = lithium.

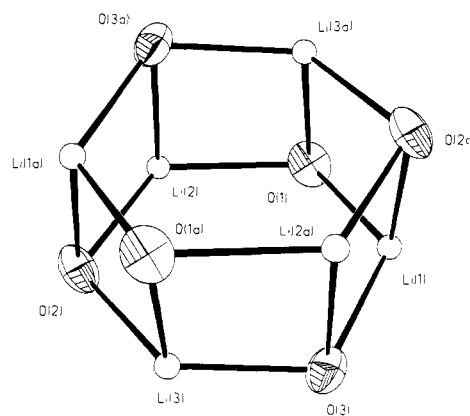


Figure 2. Selected interatomic distances and angles for one hexamer: O(1)–Li(1) = 1.869 (9); O(1)–Li(2) = 1.976 (9); O(1)–Li(3a) = 1.954 (9); O(2)–Li(2) = 1.852 (8); O(2)–Li(3) = 1.969 (10); O(2)–Li(1a) = 1.945 (9); O(3)–Li(3) = 1.809 (11); O(3)–Li(1) = 1.930 (8); O(3)–Li(2a) = 1.953(9) Å; Li(1)–O(1)–Li(2) = 111.9 (5) $^{\circ}$; Li(1)–O(1)–Li(3a) = 85.7 (4) $^{\circ}$; Li(2)–O(1)–Li(3a) = 80.9 (5) $^{\circ}$; Li(2)–O(2)–Li(3) = 113.7 (4) $^{\circ}$; Li(2)–O(2)–Li(1a) = 83.7 (4) $^{\circ}$; Li(3)–O(2)–Li(1a) = 83.5 (4) $^{\circ}$; Li(3)–O(3)–Li(1) = 117.1 (4) $^{\circ}$; Li(3)–O(3)–Li(2a) = 85.2 (4) $^{\circ}$; Li(1)–O(3)–Li(2a) = 81.5 (3) $^{\circ}$.

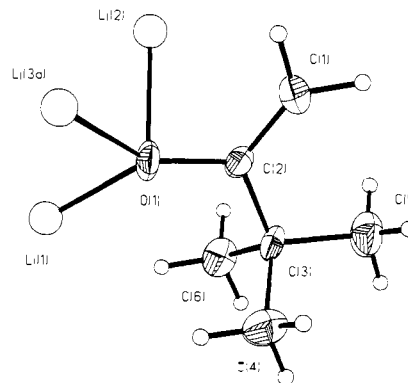


Figure 3. Selected interatomic distances and angles: C(1)–C(2) = 1.313 (8); C(2)–C(3) = 1.514 (8); C(2)–O(1) = 1.341 (5); C(1)–Li(2) = 2.420 (8); C(2)–Li(2) = 2.349 (9) Å; C(1)–C(2)–O(1) = 121.9 (5) $^{\circ}$; C(1)–C(2)–C(3) = 123.1 (4) $^{\circ}$; C(2)–O(1)–Li(1) = 140.0 (4) $^{\circ}$; C(2)–O(1)–Li(2) = 88.0 (9) $^{\circ}$; C(2)–O(1)–Li(3a) = 132.9 (4) $^{\circ}$. Selected dihedral angles: C(1)–C(2)–O(1)–Li(1) = 166.8 (12) $^{\circ}$; C(1)–C(2)–O(1)–Li(2) = 44.2 (8) $^{\circ}$; C(1)–C(2)–O(1)–Li(3a) = -31.4 (7) $^{\circ}$.

a crystallographic inversion center so that the aggregation state of the pinacolone enolate is as depicted in Figure 1, i.e., a hexamer with approximate S_6 symmetry. Two such hexameric units make

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(2) See, e.g.: House, H. O. "Modern Synthetic Reactions"; W. A. Benjamin: Menlo Park, CA, 1972; pp 492–733.

(3) X-ray diffraction analyses are reported for the following enolates or their synthetic equivalents. (a) THF-solvated enolate anions: Amstutz, R.; Schweizer, W. B.; Seebach, D.; Dunitz, J. D. *Helv. Chim. Acta* 1981, 64, 2617. (b) Zinc ester enolate (i.e., "Reformatsky reagent"): Dekker, J.; Boersma, J.; van der Kerk, G. J. M. *J. Chem. Soc., Chem. Commun.* 1983, 553. (c) β -Lithiated enamine: Polt, R. L.; Stork, G.; Carpenter, G. B.; Williard, P. G. *J. Am. Chem. Soc.* 1984, 106, 4276. (d) Lithiated *N,N*-dimethylhydrazone: Collum, D. B.; Kahne, D.; Gut, S. A.; DePue, R. T.; Mohamadi, F.; Wanat, R. A.; Clardy, J.; VanDuyne, G. *J. Am. Chem. Soc.* 1984, 106, 4865. (e) Lithiated bis(lactim) ether: Seebach, D.; Bauer, W.; Hansen, J.; Laube, T.; Schweizer, W. B.; Dunitz, J. *J. Chem. Soc., Chem. Commun.* 1984, 853. (f) Lithiated ester enolates: Seebach, D. "Proceedings of the R. A. Welch Foundation Conference", Houston, Nov 7–9, 1983. (g) **Footnote Added in Proof:** Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.*, in press.

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(b) Lochmann, L.; Lim, D. *J. Organometal. Chem.* 1973, 50, 9.

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(6) This powder was shown to be pure enolate by 60-MHz ^1H NMR spectroscopy: (CDCl_3 , Me_4Si) δ 1.12 (s, 9 H), 3.52 (s, 1 H), and 3.75 (s, 1 H). Decomposition occurred gradually over a period of 30 min in CDCl_3 solution presumably by reaction with the solvent.

(7) The unsolvated lithium enolate of pinacolone crystallized in the triclinic space group $P\bar{1}$ with unit cell parameters: $a = 11.686$ (8) Å, $b = 11.822$ (7) Å, $c = 17.144$ (17) Å, $\alpha = 80.56$ (7) $^{\circ}$, $\beta = 74.08$ (5) $^{\circ}$, and $\gamma = 66.35$ (5) $^{\circ}$. The unit cell contained a total of 12 $\text{C}_6\text{H}_{11}\text{OLi}$ units. This produces a calculated density of 1.02 g cm^{-3} for the crystal. Approximately half of the data was collected over a period of 24 h on the first crystal in a shell of $3.5^{\circ} \leq 2\theta \leq 35^{\circ}$ and the second half was collected on a second crystal spanning the range $35^{\circ} \leq 2\theta \leq 45^{\circ}$.

(8) Direct methods did not solve the structure initially because of problems associated with scaling together two data sets. This did not become apparent until a later stage of refinement. The final agreement factors are $R = 0.0883$ and $R_w = 0.0781$ for 3491 unique observed reflections and 412 independent parameters.

(9) See supplementary material for a depiction of the crystallographic asymmetric unit along with complete crystallographic parameters.

up the unit cell contents. These two hexamers are not identical but nearly so.

A less cluttered view of the hexagonal prism formed by the lithium atoms and the oxygen atoms is given in Figure 2. The six atoms forming either hexagonal face deviate by less than 0.1 Å from the best plane through the face.

Since all six enolate anions (i.e., $C_6H_{11}OLi$ units) in the crystallographic asymmetric unit of the pinacolone enolate are similar, a labeled plot of only one of these is given in Figure 3. Selected bond distances and angles for the specific enolate depicted are given with standard deviations of the least significant digits in parentheses. One salient feature is the variation in bond angles for the three C(2)-O(1)-Li bonds. Particularly outstanding are the rather large C(2)-O(1)-Li(1) bond angle (140.0 (4)°) and the small C(2)-O(1)-Li(2) bond angle (88.0 (9)°).

The average bond lengths of the six crystallographically independent enols corresponding to the bonds represented by C(1)-C(2) and C(2)-O(1) in Figure 3 are 1.33 and 1.34 Å, respectively. These values match the values of the four C=C (1.34 Å) and the four C-O (1.35 Å) bonds in the symmetrical THF-solvated pinacolone enolate.^{3a} However, a significant difference between the hexameric pinacolone enolate and the tetrameric enolate exists. This difference is exemplified by comparing average distances corresponding to C(1)-Li(2) and C(1)-Li(3a) in Figure 3. In the hexamer, the average C(1)-Li(2) distance is only 2.53 Å and the average C(1)-Li(3a) distance is 3.36 Å. For comparison, in the tetramer the average analogous distances are 3.25 and 3.28 Å, respectively. The terminal methylene carbon is ≈ 0.7 Å closer to one specific lithium atom in the hexameric aggregate. Hence, for the hexameric pinacolone enolate each π bond is paired with a unique lithium atom by virtue of a relatively short distance; whereas in the THF-solvated tetramer, the C(1)-C(2) σ bond closely bisects a Li-O-Li bond angle and C(1) is more symmetrically disposed with respect to the two staggered lithium atoms.¹⁰

Calculation of the structure of the "gas-phase" lithium enolate of acetaldehyde at the restricted Hartree-Fock level resulted in three different structures of almost identical minimum energy.¹¹ A fragment of Figure 3 represented by Li(2)-O(1)-C(2)-C(1) provides experimental realization of one of the calculated enolate geometries with a lithium atom roughly equidistant from both C(1) and C(2). The O-Li bonds are, however, ≈ 0.23 Å longer in the crystal than in the calculated structure.

The ramifications of this crystal structure for the mechanism of enolate reactions in solution remain to be determined. Evidence for the correlation of X-ray crystal structures of lithiated species with solution species exists.¹² Further investigation to establish this correlation for the hexameric pinacolone enolate as well as crystal structure analyses of additional alkali metal ketone enolates are under way.

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Registry No. *tert*-Butyl methyl ketone (lithium enolate), 70367-67-8.

(10) A similarity in both the hexameric and tetrameric enolates is the rather large bond angle of C(2)-O-Li for the one lithium that is approximately anti to C(1) and syn to C(3). Perhaps this is a consequence of the steric bulk of the *tert*-butyl group.

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Supplementary Material Available: Full crystallographic details including unit cell parameters, atomic coordinates, thermal parameters, bond lengths, bond angles, and structure factors (8 pages). Ordering information is given on any current masthead page.

Synthesis, Conformation, and Reactivity of the Rhenium Phosphide Complex ($\eta^5-C_5H_5$)Re(NO)(PPh₃)(PPh₂). The "Gauche Effect" in Transition-Metal Chemistry

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Factors that influence the conformations of metal-bound ligands are fundamentally important and can provide practical insight into reactivity, especially in metal-mediated asymmetric synthesis. Since Corey and Bailar applied concepts from organic conformational analysis to the structures of metal chelate rings over 25 years ago,¹ many steric and electronic contributions to ligand conformations have been identified.² We now wish to draw a new, stereoelectronic analogy from organic and main-group element chemistry to transition-metal chemistry—namely, that the "lone pairs" of ligating atoms should prefer to be orthogonal to the metal fragment HOMO.³ In organic and main-group inorganic compounds, this is commonly called the "gauche effect"⁴ and has a profound influence on physical^{4,5} and chemical⁶ properties.

We first sought evidence for a "gauche effect" in metal phosphide complexes (L_nMPR_2) containing pyramidal phosphorus and hence an unambiguously defined "lone pair".⁷ We noted that in Paine's crystal structure of ($\eta^5-C_5Me_5$)Fe(CO)₂(PN(CH₃)CH₂CH₂NCH₃)^{7b} the phosphorus ligand did adopt a conformation in which the lone pair was orthogonal to the iron HOMO. However, the three HOMOs of the ($\eta^5-C_5H_5$)Fe(CO)₂⁺ fragment are close in energy.^{2b,8} Hence, we synthesized rhenium phosphide complexes ($\eta^5-C_5H_5$)Re(NO)(PPh₃)(PR₂), where the metal fragment HOMO (d orbital shown in 1) would be energetically

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