^{1}H hfc's can directly be deduced. In Figure 2, bottom, the spectrum of 10-OHBChl $a^{+\cdot}$ is shown. All hfc's including their signs from General TRIPLE were assigned to molecular positions (see Table I).

When the proton in position 10 was substituted against hydroxyl, changes of the ^{1}H hfc's in the vicinity of ring V were expected. As is obvious from Table I, a predominant shift occurred for the methyl proton hfc 7 (ring III) and for the β-proton couplings 8 and 9. The latter are tentatively assigned to ring IV, rather than to ring II, due to the anticipated change in the steric interaction between the substitutents at C_{10} and C_7 (Figure 1). In the range of the small couplings 1-5 (Table I) the most prominent feature is the absence of the ^{1}H hfc 5, that was assigned to position 10 in BChl $a^{+\cdot}$. The ^{1}H hfc of the hydroxyl group, a γ-coupling, is expected to be close to zero.

Our ^{1}H hfc's 6-11 from the BChl $a^{+\cdot}$ are in excellent agreement with those reported in ref 11, the smaller ones have not been resolved in this paper (Table I). The data given in ref 12 for BChl $a^{+\cdot}$ are, however, very close to our values of the 10-OHBChl $a^{+\cdot}$ (see Table I). It is therefore proposed that the latter authors have used 10-OHBChl *a* that, presumably, was formed during a prolonged isolation and purification procedure of the bacteriochlorophyll in alcoholic solvents under aerobic conditions.[21]

The dots in the spectrum of Figure 2, bottom, indicate lines assigned to a paramagnetic byproduct[26] with a similar *g* factor. The resonances belonging to this species can be identified by General TRIPLE resonance,[10] a method that is based on the fact that ENDOR lines of a second radical in the sample show no "TRIPLE effect" when pumping transitions of the first radical. Since the starting material was free of byproducts this species must have been formed from 10-OHBChl *a* in the sample tube. The amount of the byproduct, which has not yet been identified, depends upon experimental conditions (reaction time, temperature, solvents). Pheophytinization or oxidation[5] to 10-hydroxy-2-devinyl-2-acetylchlorophyll *a* is unlikely from a comparison with the ENDOR data of such samples.[27] Due to the quite large changes in particular of the methyl hfc's in rings I and III[26] a species with an opened ring V seems to be most probable.[28] An alternative explanation is the formation of a 10-methoxylactone, which is another major byproduct of chlorophyll allomerization.[5]

Acknowledgment. This work was supported by Deutsche Forschungsgemeinschaft, Sfb 161 (W.L., F.L.) and 143 (H.S.).

Registry No. 10-OH BChl $a^{+\cdot}$, 96095-15-7; BChl $a^{+\cdot}$, 36643-16-0.

(21) The formation of 10-OHBChl *a*, sometimes even as the major bacteriochlorin, in BChl *a* isolation procuedures has been mentioned.[5,15,22] The use of alcoholic solvents like methanol for the extraction and chromatography of BChl *a* is superior to other methods because of the stabilization of the species by sixfold ligation of the central Mg that prevents the formation of certain byproducts.[22] Allomerization can be reduced to a minimum by working in dim green light with ice-cold oxygen-free solvents and by avoiding a prolonged contact.[22,23] Methanol is also an important cosolvent for the BChl *a* cation radical.[14] It should be noted that other bacteriochlorophylls, e.g., BChl *b*, are even more labile than BChl *a* and readily yield pigments of the chlorophyll spectral type.[25]

(22) Brereton, R. G.; Sanders, J. K. M. *J. Chem. Soc., Perkin Trans. 1* **1983**, 423-430, 431-434.

(23) Lubitz, W.; Isaacson, R. A.; Abresch, E. C.; Feher, G. *Proc. Natl. Acad. Sci. U.S.A.* **1984**, *81*, 7792-7796.

(24) Reference deleted in proof.

(25) Steiner, R.; Cmiel, E.; Scheer, H. *Z. Naturforsch., C* **1983**, *38C*, 748-752.

(26) The ^{1}H hfc's (MHz) of the paramagnetic byproduct are identified by ENDOR/General TRIPLE and tentatively assigned by partial deuteration:[20] methines (α,β,δ) +2.02, +2.80; γ-protons (3a,4a,7a,8a) -0.60; methyls (1a,5a) +5.52, +7.22; β-protons (3,4,7,8) +6.52, +15.62 (shoulders are observed on other lines of the main spectrum yielding 10.5, 14.3, and 16.5 MHz, two of them could belong to the remaining β-protons).

(27) Lubitz, W., unpublished results.

(28) It is the presence (and geometry) of the isocyclic ring V in chlorophylls and bacteriochlorophylls that causes the asymmetry of the spin distribution in the respective radicals. This is most obvious from the ratio of the methyl hfc's in positions 5a and 1a: opening of ring V shifts this value close to one.[29] For BChl $a^{+\cdot}$, 10-OHBChl $a^{+\cdot}$, and the byproduct radical cation this ratio is 1.96, 1.76, and 1.31, respectively.

(29) Scheer, H.; Katz, J. J.; Norris, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 1372-1381.

Simple Asymmetric Construction of Carbocyclic Framework. Direct Coupling of Dimenthyl Succinate with 1,ω-Dihalides

Akihiro Misumi, Kiyoshi Iwanaga, Kyoji Furuta, and Hisashi Yamamoto*

Department of Applied Chemistry, Nagoya University Chikusa, Nagoya 464, Japan

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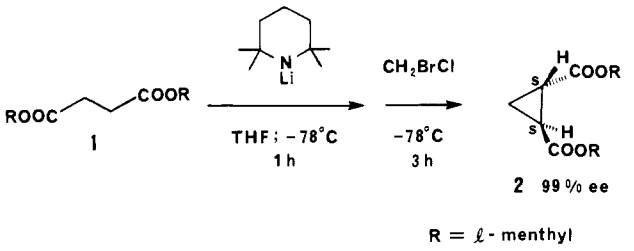
Efficient asymmetric carbocyclization processes may be one of the ultimate goals in organic synthesis. Among several potentially versatile methods, Diels-Alder reactions have been rather extensively studied, and in some cases high enantiomeric excesses were reported.[1] We have been intrigued with the possibility of the developing 2 new asymmetric annulation protocols via direct coupling of the 1,ω-dihalides and the doubly charged succinate ions.[2] The present paper describes the initial results, which show the feasibility and some limitations of this approach.

The readily available (-)-dimenthyl succinate (**1**, 7.89 g, 20 mmol)[3] in dry tetrahydrofuran (20 mL) was added dropwise at -78 °C to a solution of lithium 2,2,6,6-tetramethylpiperidide (42 mmol) in tetrahydrofuran (60 mL) under nitrogen.[4] The resulting pale yellow solution was stirred there for 1 h. The dianion thus obtained was treated with bromochloromethane (0.65 mL, 10 mmol) dropwise at -78 °C. After being stirred for 3 h at the same temperature, the reaction mixture was poured into ice-cold diluted hydrochloric acid, and the product was extracted several times with ether. The combined ether layers were washed with brine, dried over sodium sulfate, and concentrated in vacuo. The residue was subjected to column chromatography on silica gel using ether-hexane (1:19) as eluent to give (-)-dimenthyl cyclopropane-*trans*-1,2-dicarboxylate (**2**) as colorless crystals in 58%



yield (2.34 g) and in 99% de: mp 99-100 °C (after recrystallization from methanol), $[\alpha]^{25.5}_D$ +17.8° (*c* 1.0, $CHCl_3$), identical in all respects with an authentic sample.[5]

(1) A recent review: Paquette, L. A. In "Asymmetric Synthesis"; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3, Part B, Chapter 7.

(2) (a) Furuta, K.; Misumi, A.; Mori, A.; Yamamoto, H. *Tetrahedron Lett.* **1984**, *25*, 669. (b) Misumi, A.; Furuta, K.; Yamamoto, H. *Ibid.* **1984**, *25*, 671. (c) Furuta, K.; Ikeda, N.; Yamamoto, H. *Ibid.*, **1984**, *25*, 675.

(3) (-)-Dimenthyl succinate: A mixture of succinic acid (23.6 g, 0.2 mol), *l*-menthol (62.5 g, 0.4 mol), and concentrated hydrochloric acid (0.6 mL) was heated at 85-90 °C (bath temperature) for 15 h. Additional hydrochloric acid (0.6 mL) was added and the reaction mixture was heated for 15 h at the same temperature. The cooled organic layer was diluted with ether, washed with water, aqueous $NaHCO_3$, and water, and concentrated in vacuo. The residue was recrystallized from methanol to give the diester **1** as colorless crystals (33.2 g, 42%): mp 65-66 °C, $[\alpha]^{25}_D$ -88.7° (*c* 1.02, $CHCl_3$).

(4) Dienolates derived from succinate esters; see: (a) Garratt, P. J.; Zahler, R. *J. Am. Chem. Soc.* **1978**, *100*, 7753. (b) Long, N. R.; Rathke, M. W. *Synth. Commun.* **1981**, *11*, 687. (c) Bilyard, K. G.; Garratt, P. J.; Zahler, R. *Synthesis* **1980**, 389. (d) Bilyard, K. G.; Garratt, P. J.; Hunter, R.; Lete, E. *J. Org. Chem.* **1982**, *47*, 4731. (e) Girard, C.; Block, R. *Tetrahedron Lett.* **1982**, *23*, 3683. (f) Mahalanabis, K. K.; Mumtaz, M.; Snieckus, V. *Ibid.* **1982**, *23*, 3971, 3975 (1982). (g) Noire, P. D.; Franck, R. W. *Ibid.* **1982**, *23*, 1031. (h) Pohmakotr, M.; Reutrakul, V.; Phongpradit, T.; Chansri, A. *Chem. Lett.* **1982**, 687. (i) Wilkening, D.; Mundy, B. P. *Synth. Commun.* **1984**, *13*, 227; (j) *Tetrahedron Lett.* **1984**, *25*, 4619.

(5) An authentic sample was prepared as follows: Trans isomer: Matsuda, H.; Kanai, H. *Chem. Lett.* **1981**, 395. Cis isomer: Inamasu, S.; Horiike, M.; Inoue, Y. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1393.

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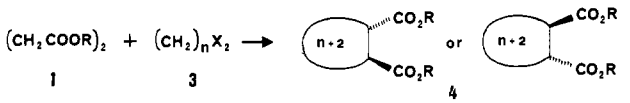
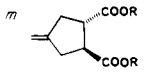
Table I. Asymmetric Syntheses of Diesters[a]



entry	1,[3] R	3 X, (equiv)	3 n	reaction conditions °C (h), addend	4 yield,[b] %	4 trans/cis[c]	4 % de[d]	4 $[\alpha]^{25}_D$[e]	4 confign
1	*l*-menthyl	Br, Cl (1)	1	−78 (3)	59	>95[5]	84		*S,S*
2	*l*-menthyl	Br, Cl (0.5)	1	−78 (3)	58	>95[5]	99	+17.8[f]	*S,S*[g]
3	*d*-menthyl	Br, Cl (1)	1	−78 (3)	60	>95	80		*R,R*
4	*l*-menthyl	Br, Cl (1)	1	−78 (3), HMPT			−33		*R,R*
5	*l*-menthyl	Br (1)	2	−78 (3), −20 (12)	73	91:9[h]			
6	*l*-menthyl	Br (0.5)	2	−78 (3), −20 (12)	(87)	93:7			
7	*l*-menthyl	Br (0.5)	2	−100 (3), −78 (1), −20 (12)	72[i]	91:9		−51.7	
8	*l*-menthyl	Br (1)	3	−78 (3)	77	>95	65		*S,S*
9	*l*-menthyl	OTs (1)	3	−78 (3)	63[i]	>95	92		*S,S*
10	*l*-menthyl	OTs (0.5)	3	−78 (3)	65[i]	>95	90	−32.8[f]	*S,S*[j]
11	*d*-menthyl	OTs (1)	3	−78 (6)	64[i]	>95	88	+33.8[f]	*R,R*
12	*l*-menthyl	Br (1)	3	−78 (3), HMPT		91:9[k]	−13		*R,R*
13	*l*-menthyl	**5**[l] (0.5)	3	−78 (3), −20 (12)	96[m]	>95	70		
14	*l*-menthyl	**5**[l] (0.5)	3	−100 (3), −20 (12)	57[m]	>95	83	−37.3	
15	*l*-menthyl	OTs (1)	4	−78 (13), −20 (12)	61	>95[n]	75		*S,S*[o]
16	*d*-menthyl	OTs (1)	4	−78 (3), −20 (12)	51	>95[n]	79	+71.7	*R,R*[o]

[a] All the reactions were carried out under nitrogen; see the experimental conditions in text. [b] Isolated yields unless otherwise specified. All new compounds gave appropriate analytical and spectral data. Yields in parentheses are yields determined on the bases of GC analyses. [c] Determined by GC analyses. [d] Unless otherwise specified, the % de was determined by GC on a 25-m PEG-HT capillary column. [e] *c* 1.0 in $CHCl_3$. [f] After recrystallization from methanol. [g] Determined by conversion to diol (DIBAH) and then to diacetate; see ref 5b. [h] Authentic sample was prepared from 1,2-cyclobutanedicarboxylic acid chloride and menthol. The cis major isomer was prepared by treatment of the sample with LDA (2 equiv) at −78 °C. [i] Excess isobutyraldehyde was added prior to workup. The unreacted enolate was quenched and the polar byproducts were readily removed by simple chromatography. [j] Determined by conversion to diol (DIBAH) and then to ditosylate: Collet, A.; Brienne, M.-J.; Jacques, J. *Bull. Soc. Chim. Fr.* **1972**, 336. [k] Authentic sample was prepared from *trans*-1,2-cyclopentanedicarboxylic acid and menthol. The cis major isomer was prepared by treatment with LDA (2 equiv) at −78 °C. [l] **5**: 3-Chloro-2-(chloromethyl)-1-propene.



[m] Cis and trans isomers were prepared separately from *cis*- and *trans*-1,2-cyclohexanedicarboxylic acid, respectively. [o] Determined by conversion to diol: Applequist, D. E.; Werner, N. D. *J. Org. Chem.* **1963**, *28*, 48.

To test the generality of the procedure, a series of 1,ω-dihalides and ditosylates were utilized in the coupling studies. As indicated in Table I, good to excellent optical yields were obtained with 3-, 4-, 5-, and 6-membered rings. Since both *l*- and *d*-menthol are available in optically pure form, this method allows the synthesis of both enantiomers of carbocyclic structures in a predictable manner.

The observed rigorous stereocontrol may be explained in the following manner. It is now well established that esters appear to give (*E*)-enolates[6] upon deprotonation with lithium diisopropylamide (LDA), regardless of the nature of the alkoxy group.[7,8] Furthermore, lithium 2,2,6,6-tetramethylpiperidide (LTMP) usually gives more (*E*)-enolate than LDA.[8] In contrast, LDA in the presence of HMPT gives mainly (*Z*)-enolate upon deprotonation.[7] To determine the enolate geometry of the dianion from **1**, the solution was quenched with excess chlorotrimethylsilane at −78 °C. The ^{1}H NMR of α-vinylic proton of crude trimethylsilyl ether showed a sharp singlet at δ 4.47 and very small peak (<5%) at δ 4.23 (CCl_4). When HMPT was present during deprotonation, the ^{1}H NMR spectra of the silylated product revealed only one singlet at δ 4.23. Thus, the reversal in enolate ratios parallels the observations noted for simple ester enolates.[9]

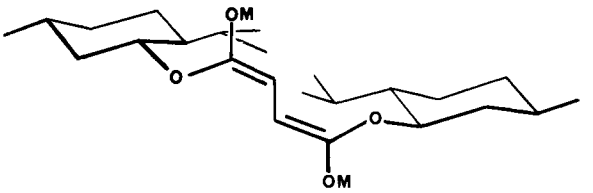


Figure 1. *s-trans*-(*E,E*)-Enolate from **1**.

The observed high stereoselectivities can be adequately explained by assuming the involvement of the crucial conformation of dianion shown in Figure 1, in which the s-trans conformation of the (*E,E*)-enolate causes an accumulating effect in chiral directing capacity of menthol. Although the (*E,E*)-enolate was found to be highly selective, giving an *S,S*/*R,R* ratio of 65–99%, the (*Z,Z*)-enolate (entries 4 and 12) was shown to be indiscriminate. This decreased selectivity may be due to the partial contribution of the chelated s-cis conformation of the (*Z,Z*)-enolate which causes the contradictory effect in chiral-directing capacity of menthol. It is evident that a detailed understanding of the stereochemical aspects of this coupling process will follow only from additional mechanistic and stereochemical studies.

We noted a slight difference in the reaction rates of the (*E,E*)- and (*Z,Z*)-enolate of **1**. Thus, the exposure of **1** with LDA generated a mixture of (*E,E*)- and (*Z,Z*)-enolate (ca. 2:1), which was treated with bromochloromethane at −78 °C for 3 h and then with excess chlorotrimethylsilane. The ^{1}H NMR analysis of the crude product revealed a single peak at δ 4.23 of the (*Z,Z*)-ketene acetal from the unreacted enolate. The higher reactivity of

(6) The *E*/*Z* notational format of Evans, see p 11 of ref 1. Thus, the highest priority designation is always assigned to the OM group, independent of the metal.

(7) Ireland, R. E.; Muller, R. H.; Willard, A. K. *J. Am. Chem. Soc.* **1976**, *98*, 2868. See also: Chan, T. H.; Aida, T.; Lau, P. W. K.; Gorys, V.; Harpp, D. N. *Tetrahedron Lett.* **1979**, 4029.

(8) For a general review of enolate geometry, see: Evans, D. A.; Heathcock, C. H. In "Asymmetric Synthesis"; Vol. 3, Part B"; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3, Part B, Chapter 1 and 2, respectively. Heathcock, C. H. In "Comprehensive Carbanion Chemistry"; Buncel, E., Durst, T., Eds.; Elsevier: Amsterdam, 1984; Part B.

(9) The *E,Z* isomer was not detected by ^{1}H NMR analyses.

(*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

Paul G. Williard* and Gene B. Carpenter

Department of Chemistry, Brown University
Providence, Rhode Island 02912
Received December 26, 1984

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 analyses[3] 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 °C following a procedure slightly modified from that reported.[5] These crystals remain suitable for diffraction analysis if they are kept below −5 °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 °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 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

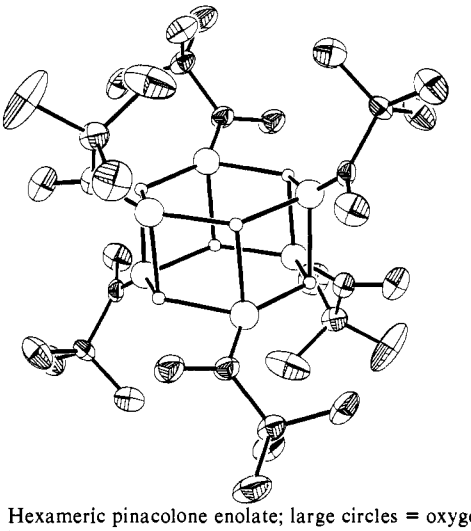


Figure 1. Hexameric pinacolone enolate; large circles = oxygen, small circles = lithium.

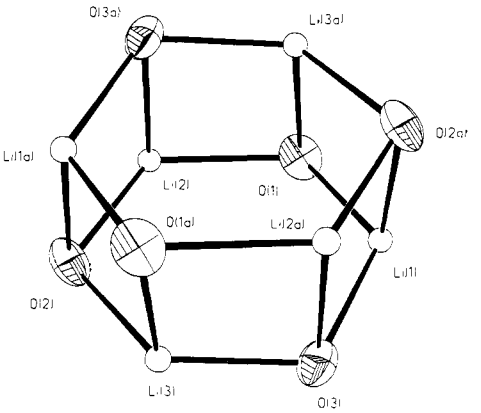


Figure 2. Selected interatomic distances and angles for one hexamer: O(1)–Li(1) = 1.869 (9); O(1)–Li(2) = 1.976 (9); O(1)–Li(3a) = 1.954 (9); O(2)–Li(2) = 1.852 (8); O(2)–Li(3) = 1.969 (10); O(2)–Li(1a) = 1.945 (9); O(3)–Li(3) = 1.809 (11); O(3)–Li(1) = 1.930 (8); O(3)–Li(2a) = 1.953(9) Å; Li(1)–O(1)–Li(2)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

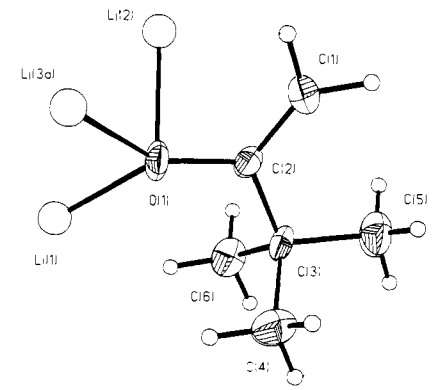


Figure 3. Selected interatomic distances and angles: C(1)–C(2) = 1.313 (8); C(2)–C(3) = 1.514 (8); C(2)–O(1) = 1.341 (5); C(1)–Li(2) = 2.420 (8); C(2)–Li(2) = 2.349 (9) Å; C(1)–C(2)–O(1) = 121.9 (5)°; C(1)–C(2)–C(3) = 123.1 (4)°; C(2)–O(1)–Li(1) = 140.0 (4)°; C(2)–O(1)–Li(2) = 88.0 (9)°; C(2)–O(1)–Li(3a)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

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

(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.

(4) (a) Rathke, M. W.; Sullivan, D. F. *J. Am. Chem. Soc.* **1973**, *95*, 3050. (b) Lochmann, L.; Lim, D. *J. Organometal. Chem.* **1973**, *50*, 9.

(5) Lochmann, L.; De, R. L.; Trekoval, J. *Organomet. Chem.* **1978**, *156*, 307.

(6) This powder was shown to be pure enolate by 60-MHz ^{1}H 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, α = 80.56 (7)°, β = 74.08 (5)°, and γ = 66.35 (5)°. The unit cell contained a total of 12 $C_6H_{11}OLi$ units. This produces a calculated density of 1.02 g cm^{-1} for the crystal. Approximately half of the data was collected over a period of 24 h on the first crystal in a shell of $3.5° \leq 2\theta \leq 35°$ and the second half was collected on a second crystal spanning the range $35° \leq 2\theta \leq 45°$.

(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.

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