a sample of crude product (3.2 g) gave a-IVb-n (1.4 g). ^{1}H NMR: δ 6.55 (dd, $J = 6, 3$ Hz, 1 H, H-5), 6.10 (dd, $J = 6, 3$ Hz, 1 H, H-6), 4.30 (d, $J = 7.9$ Hz, 1 H, C*H*(OMe)$_2$), 3.33 (s, 3 H, OMe), 3.34 (s, 3 H, OMe), 3.03 (m, 2 H, H-1, H-4), 2.70 (bd d, $J = 7.9$ Hz, 1 H, H-7), 2.07 (ddd, $J = 9.5, 4.7$ Hz, $\{3.2\}_{3.0}$, 1 H, H-3 exo), 1.64 (m, 2 H, CH$_2$), 1.27 (m, 8 H), 0.87 (bd t, $J = 7$ Hz, 3 H, Me). ^{13}C NMR: δ 215.66 (e, C-2), 141.77 (o, C-5), 130.57 (o, C-6), 101.87 (o, CH(OMe)$_2$), 62.76 (o, C-7), 57.97 (o, C-1), 54.51 (o, OMe), 52.33 (o, OMe), 44.13 (o, C-3/C-4), 44.06 (o, C-3/C-4), 32.08, 31.63, 29.15, 27.98 (all e), 22.58 (e), 14.05 ppm (o, Me).

Preparation of *exo*-3-Hexyl-*syn*-7-(dimethoxymethyl)bicyclo[2.2.1]hept-5-en-2-one (s-IVb-x). Procedure B. *syn*-7-(Dimethoxymethyl)bicyclo[2.2.1]hept-5-ene-2-one^{1,3} (s-I; 20 g, 0.11 mol) and 1,1-dimethylhydrazine (6.7 g, 0.11 mol) were heated together at 70 °C for 1 h, and the product was isolated by vacuum distillation (bp 100 °C (0.5 mm)) to give dimethylhydrazone (s-I-D) (16.4 g, 66%), 3:2 mixture of *E* and *Z* isomers. ^{1}H NMR: δ 6.25 (m, 1 H), 6.07 (m, 1 H), 4.35 and 4.33 (d 2:3 ratio, 1 H total), 3.90 (m, 2.5 H), 3.30 (two s, 6 H, OMe), 3.00 (m, 1.5 H), 2.45 (two s, 6 H, NMe$_2$), 2.30–1.80 (m, 3 H). ^{13}C NMR: major, δ 171.7, 137.1, 129.9, 102.4, 63.6, 53.4, 52.7, 52.0, 48.3, 42.6, 33.6; minor, δ 171.8, 137.8, 128.9, 102.4, 63.0, 53.2, 53.1, 48.2, 47.1, 41.6, 35.0. Alkylation with hexyl iodide was carried out on a 0.03–0.07-mol scale by procedure B at −30 to −40 °C for 3 h to give s-VIb-x in 60–80% yield after FCC (4:1, P/E). ^{1}H NMR: δ 6.23 (dd, $J = 6, 3$ Hz, 1 H, H-5), 6.05 (dd, $J = 6, 3$ Hz, 1 H, H-6), 4.35 (d, $J = 8$ Hz, 1 H, CH(OMe)$_2$), 3.30 (s, 6 H, OMe), 3.15 (m, 1 H, H-1/H-4), 2.85 (m, 1 H, H-1/H-4), 2.50 (bd d, $J = 8$ Hz, 1 H, H-7), 2.45 (s, 6 H, NMe$_2$), 1.40–1.20 (m, 11 H), 0.90 (bd t, 3 H, Me). ^{13}C NMR: δ 174.47 (s, C-2), 137.37 (d, C-5), 131.29 (d, C-6), 102.50 (d, *C*H(OMe)$_2$), 58.81 (d, C-7), 52.93 (q, OMe), 51.94 (d, C-1), 46.80 (q, NMe$_2$), 46.56 (d, C-3/C-4), 45.52 (d, C-3/C-4), 31.83, 29.21, 28.96, 28.79, 22.68 (all t, CH$_2$), 14.04 (q, Me). Hydrolysis with 1% HCl gave *exo*-3-hexyl-*syn*-7-(dimethoxymethyl)bicyclo[2.2.1]hept-5-en-2-one, s-IVb-x, in 63% yield after FCC (4:1, P/E). ^{1}H NMR: δ 6.50 (dd, $J = 6, 3$ Hz, 1 H, H-5), 6.05 (m, 1 H, H-6), 4.45 (d, $J = 8$ Hz, 1 H, C*H*(OMe)$_2$), 3.32 (s, 3 H, OMe), 3.28 (s, 3 H, OMe), 2.98 (m, 2 H, H-1, H-4), 2.70 (bd d, $J = 8$, 1 H, H-7), 2.05–1.70 (m, 1 H, H-3 endo), 1.30 (m, 1 H, CH$_2$), 0.88 (bd t, 3 H, Me). ^{13}C NMR: δ 214.94 (s, C-4), 141.28 (d, C-5), 128.51 (d, C-6), 101.96 (d, *C*H((OMe)$_2$), 60.62 (d, C-7), 57.53 (d, C-1), 53.24 (q, OMe), 53.07 (q, OMe), 47.51 (d, C-3/C-4), 45.61 (d, C-3/C-4), 31.66, 30.20, 29.17, 28.38, 22.62 (all t, CH$_2$), 14.06 (q, Me).

Preparation of *exo*-3-*n*-Hexylbicyclo[2.2.1]heptan-2-one. A solution of the enolate of bicyclo[2.2.1]heptan-2-one (VII; 0.01 mol) in THF (30 mL) was prepared and alkylated with *n*-hexyl iodide (2.6 g, 0.12 mol) by procedure A with overnight reaction. FCC (20:1, P/E) gave VII (1.25 g, 73%). ^{1}H NMR: δ 2.6–2.40 (m, 2 H), 1.95–1.15 (m, 18 H), 0.88 (bt, 3 H). ^{13}C NMR: δ 220.15 (s, C-2), 54.13 (d, C-3), 49.55 (d, C-4), 39.29 (d, C-1), 34.83 (t, C-7), 31.72, 29.23, 29.15, 28.32, 28.06 (all t, CH$_2$, C-5), 24.14 (t, C-6), 22.65 (t, CH$_2$), 14.07 (q, Me).

Acknowledgment. NSF Grant 79-16831 and Eli Lilly provided support for this work. Their contribution is acknowledged with gratitude.

Registry No. (±)-I-D (isomer 1), 104323-59-3; (±)-I-D (isomer 2), 104323-60-6; (±)-a-I, 73650-17-6; (±)-s-I, 54094-16-5; (±)-s-I-D (isomer 1), 104323-76-4; (±)-s-I-D (isomer 2), 104323-77-5; (I)-(II) (aldol dimer), 104323-62-8; (aIa)-(aII) (aldol dimer), 104323-74-2; (I)-(IIIa-x) (aldol dimer), 104323-82-2; (±)-III, 104323-61-7; (±)-IVb-x, 104323-66-2; (±)-IVc-n, 104323-71-9; (±)-IVc-x, 104323-70-8; (±)-IVd-x, 104323-67-3; (±)a-IVa-n, 104323-72-0; (±)a-IVa-x, 104323-73-1; (±)a-IVb-n, 104323-75-3; (±)s-IVb-x, 104323-79-7; Vb, 104323-68-4; (±)-Vc, 104323-69-5; Vd, 104323-81-1; (±)VI-a, 104323-63-9; (±)VI-b, 104323-64-0; (±)VI-d, 104323-65-1; (±)-s-VIb-x, 104323-78-6; (±)VII (enolate), 104323-80-0; (±)VIIb-x, 104335-66-2; (±)-norbornenone, 51736-74-4; 1,1-dimethylhydrazine, 57-14-7; propanal, 123-38-6; methyl iodide, 74-88-4; *n*-hexyl iodide, 638-45-9; benzyl chloride, 100-44-7; allyl bromide, 106-95-6.

Supplementary Material Available: Tables of ^{13}C shifts of substituted norbornanes and illustrations of spectral data of norbornenones substituted at the 7-position (16 pages). Ordering information is given on any current masthead page.

Structure and Dynamic Behavior of the Lithium Enolate of Acetaldehyde in Solution

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Proton, ^{13}C, and ^{7}Li nuclear magnetic resonance spectroscopy and studies of spin–lattice relaxation times have been used to investigate the nature of the simplest enolate, the lithium enolate of acetaldehyde 1 in tetrahydrofuran. The methine carbon relaxes seven times more slowly than the methylene, but both show a full nuclear Overhauser effect. The methylene carbon relaxes even more rapidly than lithium—a quadrupolar nucleus. Two similar species exist in THF but the equilibrium is only slightly temperature-sensitive. The exchange is slow on the NMR scale at low temperature. These results indicate that lithium enolate 1 exists as a tetramer with a rotational barrier of only 6.6 ± 1 kJ/mol for rotation of the vinyl group about the C–O bond.

Alkali-metal enolates are widely used in synthetic organic chemistry as a form of nucleophilic carbon, and a very large number of reactions involve them as intermediates.[1,2] Enolates are ion-paired with alkali-metal ions in solution and tend to form aggregates in nonpolar solvents and weakly polar solvents which can solvate cations. The reactivities of enolate ions are directly related with their solution structures.[2,3] The structure of enolates has been the subject of much recent X-ray work,[4] but struc-

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tural information about the forms present in solution remains quite limited.

^{13}C NMR spin–lattice relaxation times T_1 provide insight into dynamic behavior of organic molecules in solution. The analysis of T_1's for individual carbons of a molecule gives information on both overall molecular motion and fast internal rotations[5] and thus on associations between solute–solute and/or solute–solvent. Jackman and coworkers have characterized the structures of phenoxides,[6] amides,[7] lithioisobutyrophenone aggregates,[8] and phenyllithium[9] in ether solvents through T_1 measurements. This novel approach offers some advantages over the usual measurements of colligative properties in that it identifies the dominant solution species, is applicable over a large temperature range, and can be used to determine the sizes of individual molecular or aggregate species in a mixture. For compounds which undergo decomposition the superiority of the T_1 method is far more obvious.

The ^{13}C and ^{7}Li NMR spectra and relaxation times of the lithium enolate of acetaldehyde **1** in THF and THF/*n*-hexane mixed solvents have been measured in the temperature range −80 to 0 °C. The spin–lattice relaxation times of the two vinyl carbons provide not only the direct experimental evidence for isotropy or anisotropy of overall molecular motion but also the establishment of its internal mobility and solution structure.

Experimental Section

Preparation of Lithium Enolate 1 Solutions. Lithium enolate **1** was indirectly synthesized by the reaction of *n*-butyllithium and THF.[10] A three-neck flask with one-neck extended to incorporate a medium porosity sintered glass disk was used for the preparation. An appropriate amount of *n*-BuLi in *n*-hexane (Alfa) was added via syringe at −78 °C to the flask containing dry THF. The mixture was then allowed to stir at room temperature until aliquots showed no *n*-Buli by ^{1}H NMR ($\delta \sim -1$). The reaction was run under a nitrogen stream and the ethylene (δ 5.3) swept out. The desired lithium enolate **1** was formed in essentially quantitative yield based on *n*-BuLi. Lithium enolate **1** of different concentrations in solution of various molecular ratios of THF and *n*-hexane could be prepared by using *n*-BuLi solutions of different concentrations and by adjusting the nitrogen stream. When enolate **1** in THF or other pure ether solvents was needed, the liquid was decanted through the lengthened neck after the reaction solution was cooled to −78 °C, and the crystals of enolate **1** were recrystallized in THF, washed several times with *n*-hexane, and then dissolved in the required solvent. The solution for NMR experiments was transferred to dry 5 and 8-mm NMR tubes via syringe and were vacuum degassed by using the freeze–pump–thaw technique and sealed. All solutions prepared by this method showed <1% impurities by NMR and were stable at low temperature for several months. Concentrations of the enolate and molar ratios of THF and *n*-hexane were measured by ^{1}H NMR.

NMR Spectroscopy. ^{1}H (200 MHz), ^{13}C (50.3 MHz), and ^{7}Li (77.7 MHz) NMR spectra were taken on Varian XL-200 spectrometer. Two NMR tubes were inserted coaxially with the sample in the inner tube. CH_3OH-d_4 was used as a lock signal in the outer tube. ^{13}C and ^{7}Li relaxation times were determined by using 180°–τ–90° pulse sequences.[11] Seven and eleven randomly ordered τ values were used in each determination, and data were processed by nonlinear least-squares routine provided by the XL-200 software. At least two measurements for each T_1 were made. NOE measurements were made by comparison of noise-decoupled spectra with spectra obtained with the decoupler on only during data acquisition. A proton magnetization recovery delay larger than $5T_1$ was employed. NMR probe temperatures were controlled by spectrometer software and measured with an NMR thermometer: a coaxial tube containing a 50:50 v/v mixture of acetone-d_6 and carbon tetrachloride.[12]

Table I. ^{13}C Chemical Shifts (ppm)[a] of Lithium Enolate 1 (1.2 M) in THF and in THF/Hexane

T, °C	C-1			C-2		
−84	157.94[b]	158.40[c]	157.82[d]	81.03[b]	80.29[c]	81.08[d]
−64	157.93	158.39	157.82	81.00	80.26	81.05
−48	157.93	158.34	157.82	80.96	80.23	81.04
−38	157.92	158.31		80.94	80.23	
−33	157.93		157.82	80.94		81.00
−9	158.02		157.84	80.81		80.96
9			157.86			80.93

[a] Referred to the upfield signal of THF (δ 25.30). [b] Major component (75%) in THF. [c] Minor component (25%) in THF. [d] THF/hexane (2.2:1).

Results and Discussion

NMR Spectral Data. ^{13}C NMR chemical shifts of the enolate should reflect its structure in solution. Any substantial change in the structure of an ion pair or its aggregate will cause a change in the electron distribution of the ambident anion, particularly at carbon 2.[8,13] ^{13}C NMR spectra of the lithium enolate **1** were measured in THF and THF/*n*-hexane mixed solvents between −90 and 10 °C. (Table I) Two species of enolate **1** were detected in THF. The ratio of the two species is about 3:1 according to integration. The ^{13}C NMR signal line widths of two components were comparable at −84 °C and became broad as temperature was increased with enhanced broadening of the minor component. These results indicate an equilibrium between two species with slow exchange on the NMR time scale (<100 s^{-1}) below −38 °C. The coexistence of two exchanging species was also seen in the ^{1}H NMR spectra of H_E. The H_E multiplet of the minor component was on the upfield side of that of the major with a chemical shift difference of 0.062 ppm. The coexistence of two species in THF/*n*-hexane was also observed in some instances, which depended on concentration of enolate **1** and the ratio of THF and *n*-hexane. The variations in ^{13}C chemical shifts of both species were less than 0.1 ppm in all solutions. The chemical shifts of samples in THF/*n*-hexane where only a single species was observed at low temperatures were the same within 0.1 ppm as those of the major form in THF and other THF/*n*-hexane mixtures. These observations indicate that the basic structures of major and minor forms are almost identical. Furthermore the fact that the ^{13}C chemical shift difference between major and minor species was less than 0.7 ppm strongly suggests that both have the same degree of aggregation because change in degree of aggregation produces

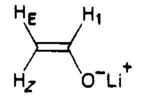

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Table II. Relaxation Times (T_1, s) and nOes of Lithium Enolate 1 and THF[a]

	enolate 1[b]						
	C-1		C-2			THF, T_1	
T, °C	T_1	nOe[d]	T_1	nOe	^{7}Li[c]	C_α	C_β
−64	1.96	2.3	0.24	2.5	0.40	5.3	8.4
−48	2.53	2.5	0.35	2.6	0.57	6.3	9.4
−1	5.19	2.7	0.71	2.7		10.5	13.9

[a] 1.2 M lithium enolate 1 in THF. [b] Major component except those at −1 °C. [c] Sample in THF containing small amount of *n*-hexane. [d] nOe ± 10%; T_1 ± 5%.

larger enolate shifts. Jackman et al. have observed 1.6 and 4.6 ppm differences at C-1 and C-2 between dimer and tetramer of lithioisobutyrophenone in dimethoxyethane[8] and 6 and 3 ppm shift differences at the para position of lithium phenoxide between tetramer, dimer, and monomer. House and co-workers[13] have observed similar results for the enolate of phenylacetone.

Lithium enolate 1 had spin–spin coupling constants of $^1J_{C1H}$ = 156.6 Hz and $^1J_{C2H}$ = 152.5 Hz (H_E's and H_Z's not resolved), typical values for sp^2 carbons. Thus both coupling constants and ^{13}C chemical shifts indicate double-bond character of the C-1–C-2 bond of lithium enolate 1 with negative charge being localized to a large extent on oxygen. The result is consistent with previous IR, ^{1}H NMR, and X-ray studies.[14-16]

Carbon-13 Spin–Lattice Relaxation Times. The measured ^{13}C spin-lattice relaxation times and nOes for lithium enolate 1 in THF at different temperatures are shown in Table II together with those of THF.

Relaxation for carbons bearing directly bonded hydrogen is dominated by dipole–dipole interaction

$$\frac{1}{T_1^{\mathrm{DD}}} = \sum_i \left(\frac{\mu_0}{4\pi}\right)^2 h\gamma_C^2\gamma_H^2 r^{-6}{}_{\mathrm{C-H}_i}\tau_c \qquad (1)$$

where μ_0 is the vacuum permeability, γ_H and γ_C are the magnetogyric ratios for ^{1}H and ^{13}C, respectively, $r_{\mathrm{C-H}}$ is the effective carbon–hydrogen internuclear distance, and τ_c is the rotational correlation time for each C–H dipole.[17] Equation 1 applies for small molecules undergoing rapid reorientation such that the extreme narrowing condition, $\omega^2\tau_c^2 << 1$, is satisfied. Dipolar relaxation generates a nuclear Overhauser effect (nOe). C-1 and C-2 show a full nOe which confirms the dipolar relaxation mechanism. For molecules which reorient isotropically, τ_c, for each C–H dipole, can be calculated with sufficient accuracy using the Stokes–Einstein model with the Gierer–Wirtz empirical factor f_{GW}[8,18]

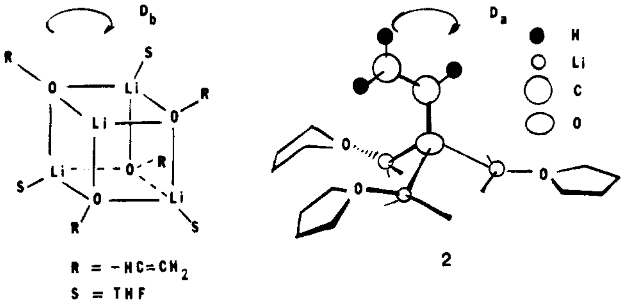
$$\tau_c = Vf_{\mathrm{GW}}\eta/kT = 4\pi r_0^3 f_{\mathrm{GW}}\eta/3kT \qquad (2)$$

where η is the solution viscosity, $V = 4\pi r_0^3/3$ is the volume of the solute molecule, and f_{GW} depends on the ratio of solvent to solute radius r_s/r_0:

$$f_{\mathrm{GW}}^{-1} = 6(r_s/r_0) + (1 + r_s/r_0)^{-3} \qquad (3)$$

The two carbons in enolate 1 both have shorter T_1 values than those of THF. These small T_1 values show that the enolate 1 is not monomeric and must form an aggregate which is significantly larger than a THF molecule. The methine carbon relaxes seven times more slowly than the methylene. The difference in relaxation times is too great to ascribe to the number of attached protons or change in C–H bond length. The difference must be a correlation time, τ_c, phenomenon resulting from differential motion of C–H dipoles, otherwise the T_1 of carbon-1 should only be twice as large as that of carbon-2 (cf. eq 1).

Aggregation and Differential Motion. The motional anisotropy indicated by the T_1 values requires fast rotation of the C-1–H dipole and slow rotation of at least one of the C-2–H dipoles. This is nicely accommodated in a tetrameric aggregate, and the solvated tetrameric structure 2 is proposed with essentially free rotation of the vinyl group about the C-1–O axis. Such differential C–H motion is only possible in an aggregate of 1. In a monomer, each C–H dipole has essentially the same orientation with the principal rotation axis of the enolate. Similar behavior has been observed in the tetramer of lithium phenoxide where the para carbons relax more rapidly than the ortho and meta carbons.[6] The influence of differential rotation on correlation times has been treated by Woessner.[19] When a molecule has two rotational diffusion constants, the correlation time of a C–H dipole which makes an angle, θ, to the major rotation axis of molecule is given by



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$$\tau_c = \frac{(3\cos^2\theta - 1)^2}{24D_b} + \frac{3\cos^2\theta\,(1-\cos^2\theta)}{5D_b + D_a} + \frac{3(1-\cos^2\theta)^2}{4(2D_b + 4D_a)} \qquad (4)$$

where D_a and D_b are the rotational diffusion constants around the major and minor rotation axes, respectively. The extreme narrowing condition is assumed. This leads to the important corollary that in a rigid molecule with equal C–H bond lengths, the T_1 times are controlled by the rotational direction cosines. For a spherical molecule, $D_a = D_b$, and eq 4 reduces to eq 5 for any angle θ:

$$\tau_c = 1/6D_a \qquad (5)$$

The relaxation of enolate 1 is then determined by the overall tumbling of the aggregate and the internal rotation of the vinyl group. Faster rotation means less efficient relaxation and longer T_1. The C-2–H_E bond is essentially colinear with the C-1–O bond, and the latter points toward the center in the approximately spherical aggregate. The internal motion, D_a, therefore does not have any influence on the correlation time of the C-2–H_E dipole (eq 4) and so is equal to that of the overall tumbling of aggregate (τ_0). ^{7}Li relaxation is governed by the same tumbling. For the C-1–H dipole, rotation around the C-1–O bond reduces its effective correlation time. The C-2–H_Z dipole makes the same contribution to relaxation of carbon-2 as C-1–H

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Table III. Volume and Dynamic Behavior of Lithium Enolate 1 Aggregate in THF[a]

T, °C	T_1 (C-2), s	T_1 (C-2–H_E) s	$10^{10}\tau_0$, s	$10^2\eta$, p	f_{GW}	r_0, Å	$10^{11}\tau_i$, s	α[b]
–64	0.24	0.27	1.54	1.67	0.32	5.85	1.69	9.1
–48	0.35	0.41	1.04	1.25	0.31	5.81	1.38	7.5
–1	0.71	0.82	0.51	0.61	0.33	6.11	0.67	7.6

[a] Data for major component except those at –1, computed by using an effective C-2 –H_E internuclear distances of 1.07 Å. [b] $\alpha = \tau_0/\tau_i$

dipole does to carbon-1 as θ is about 120° for both.[20] Thus C-2–H_E dipole's contribution to relaxation of 2-carbon is

$$\frac{1}{T_1(\text{C-2–H}_E)} = \frac{1}{T_1(\text{C-2})} - \frac{1}{T_1(\text{C-2–H}_Z)} \qquad (6)$$

with T_1 (C-2–H_Z) = T_1 (1).

The T_1(C-2–H_Z), then, can be used to calculate the effective radius r_0 of the aggregate of enolate 1 by eq 1–3 since the T_1(C-2–H_E) is independent of internal rotation. With a value of $r_{\text{C-H}}$ = 1.07 Å, eq 1 becomes

$$r_0^3 = 1.38 \times 10^{-27} T/\eta f_{GW} T_1(\text{C-2–H}_E) \qquad (7)$$

where r_0 and η are in centimeters and poise, respectively. The viscosity of the sample was not measured but can be assumed to be equal to that of the pure solvent for current purpose. Freeman[21] has generated an empirical equation for estimation of THF viscosity as a function of temperature. The value of f_{GW} can be obtained in iterative fashion. First T_1(C-2–H_E) was used to evaluate r_0 by assuming f_{GW} = 1. This value of r_0 and the a value of the solvent radius r_s = 2.79 Å based on Van der Waals volumes[22] were then used in eq 3 to obtain an improved value of f_{GW}. Iteration rapidly converged on the values of r_0 and f_{GW} given in Table III. As $\omega^2\tau_0^2 \approx 10^{-4}$, the extreme narrowing assumption is valid.

The major species has almost the same effective radius at different temperatures in the experimental range. This result strongly suggests that the major species has the same degree of aggregation in the temperature range measured. The value of r_0 at 1 °C is about 4% larger, comparable to our experimental error, but it may indicate that the minor species, which rapidly exchanges with the major one at this temperature, is slightly larger than the major one. The maximum and minimum radii of structure 2 determined from models are 6.4 and 5.4 Å, respectively, which were obtained by using hydrogen van der Waals radii, standard carbon–carbon and carbon–oxygen bond lengths, and a value of 2.0 Å for the Li–O ionic bond.[4,16] The effective radius of structure 2 is consistent with the value of 5.8 Å obtained from the NMR data.

The precision of the relaxation data for the minor component was not as good as those for the major one because of broader signals and poorer signal/noise. The minor species relaxed faster than the major by less than 5%, for instance, 1.92 and 0.24 s at –64 °C (cf. Table II). Though the differences in relaxation times were below experimental accuracy, all data were consistently smaller than those for the major species. This suggests that the minor species is slightly larger. Such a small difference is not expected to arise from variation in the degree of aggregation in agreement with the data from ^{13}C chemical shifts. Therefore, the minor component is postulated to be a solvated nonrigid cubic tetramer in THF. The difference between the major and minor tetramers presumably reflects a variation in degree of solvation. The data do not warrant further speculation, and the exact structure remains ambiguous. In various THF/n-hexane mixtures the ^{13}C chemical shifts were close to those in THF and the factor of 7 differential in relaxation times was maintained. The solvated tetramer **2** is also present in these mixed solvents.

Dynamic Behavior of the Aggregate in Solution. According to the nonrigid tetramer model the aggregate as a whole reorients isotropically with a rotational diffusion constant, D_0 and a correlation time, $\tau_0 = 1/6D_0$. The vinyl group has an additional internal rotation with a diffusion constant D_i and internal correlation time τ_i. This can be defined in terms of D_i as $\tau_i \equiv 1/2D_i$ where D_i represents a one-dimensional process.[23] Thus the nonrigid tetramer has two rotational diffusion constants: $D_a = D_0 + D_i$ and $D_b = D_0$. For C-1–H and C-2–H_Z dipoles (θ = 120°) their correlation times are identical and given (eq 4) by

$$\tau_c = \tau_0[1/64 + (1 + (\alpha/2)^{-1}9/16 + (1 + 2\alpha))^{-1}27/64] \qquad (8)$$

with $\alpha = \tau_0/\tau_i$. Using T_1 (C-1) and T_1 (C-2–H_E), values of α and τ_i were calculated (Table III). The vinyl group rotates nine times as fast as overall reorientation at –64 °C. It is this internal rotation that makes the significant difference in relaxation properties of the two carbons of lithium enolate 1. This is the first observation, to our knowledge, that there is fast rotation about the C–O axis in a lithium enolate. Lithium phenoxide shows the same property.[6] Both overall and internal rotations became faster as the temperature was raised, as reflected in the decreasing correlation time. Overall motion was more temperature sensitive than internal rotation. Activation energies were estimated from the Arrhenius equation

$$\tau_c = \tau_c^0 \exp(E_a/RT) \qquad (9)$$

and found to be 8.5 ± 0.7 kJ·mol^{-1} for overall orientation and 6.6 ± 1.0 kJ·mol^{-1} for internal vinyl group rotation. The values are consistent with classical rotational diffusion as is the constancy of $\eta T_1/T$.

Li Quadrupole Splitting Constant (QSC). This parameter, QSC = $(1 + \eta^2/3)^{1/2}(e^2Qq_{zz}/h)$ where $\eta = (q_{zz} - q_{xx})/q_{yy}$ and q_{ii} are the elements of the electric field gradient tensor, has been used by Jackman[6–9] to study the local electronic environment around the lithium cation. The QSC (kHz) can be determined from ^{7}Li spin–lattice relaxation time using the equation

$$1/T_1(^7\text{Li}) = (2\pi/5)(\text{QSC})^2\tau_c \qquad (10)$$

The term τ_c is the correlation time for reorientation of the principal axis of the electric field gradient tensor which is assumed to be the correlation time for tetramer reorientation, τ_0, determined from ^{13}C dipolar relaxation above. Substitution in eq 10 gives a QSC of 65 kHz. This is directly comparable with the value of 66 kHz for lithium phenoxide tetramer in dimethoxyethane but a factor of 2 smaller than for lithium isobutyrophenone enolate (IBP) (Table IV).[24] Ortho substituents in lithium phenoxides

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J. Org. Chem. **1986**, *51*, 4224–4232

Table IV. ^{7}Li Quadrupole Scalar Coupling Constants for Enolates and Phenoxides in Ether Solvents (kHz)

	form[a]	THF	dioxolane	$MeOCH_2$-CH_2OMe	ref
I	T	65			this work
LiIBP[b]	T	136	133	178	8
LiOPh	T		69	66	6
IOPh (2,6-Me_2)	D		147	154	6
LiOPh (2,6-di-*t*-Bu)	M		212		6

[a] T = tetramer; D = dimer; M = monomer. [b] Lithium isobutyrophenone enolate.

resulted in comparable changes which were correlated with the change in electronic environment of the cation on conversion of tetramer to dimer and monomer. Two plausible explanations for the variation in lithium QSC between these two enolates are that the increased bulk of IBP increases the Li–solvent distance producing a more anisotropic electronic environment or that IBP is undergoing rapid internal rotation in the tetramer. Since the para C–H dipole and the Li–O quadrupole axis are not parallel, rapid internal rotation would lead to an apparently smaller τ_c and produce a larger QSC on substitution in eq 10.[24] Both effects may be operating.

Conclusion

The simplest lithium enolate 1 has been shown to exist as a solvated tetramer in THF solution–structure 2. Remarkably, it is found that the enolate rotates more rapidly about its C–O axis than the aggregate reorients in solution. Lithium phenoxide behaves analogously, and the analogy is strengthened by the finding that the electronic environment around the lithium cation is the same in both compounds as reflected in their equivalent quadrupole scalar coupling constants. The structure of 1 in THF should thus be written

$$(CH_2{=}CHOLi)_4$$

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Comparison of Molecular Bromine and Tribromide Ion as Brominating Reagents. 2. Kinetic and Product Investigation of the Bromination of 3-Substituted Cyclohexenes

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The kinetics and products of bromination of several 3-substituted cyclohexenes with molecular Br_2 and with tetrabutylammonium tribromide have been investigated in 1,2-dichloroethane and chloroform. In both solvents the reactions of the unsubstituted, 3-alkyl-substituted, and 3-halogen-substituted olefins followed a third-order rate law (second order in Br_2). Changing the solvent from 1,2-dichloroethane to chloroform caused a 13- to 41-fold decrease in k_3. A *tert*-butyl group produced a 6- or 3-fold deceleration in k_3 in the two solvents, whereas a 3-bromo or 3-chloro substituent reduced the k_3 by five orders of magnitude. Tetrabutylammonium tribromide reacted with all investigated substrates following a second-order rate law in both solvents. Added bromide had no significant effect on the rates nor on the products. These reactions were 6- to 18-fold faster in chloroform than in 1,2-dichloroethane. A *tert*-butyl group caused a 35- to 36-fold decrease, a 3-bromo and a 3-chloro substituent an about three orders of magnitude decrease, and a benzoyloxy or para-substituted benzoyloxy group an about two orders of magnitude decrease in k_2. The products of the molecular Br_2 reactions consisted of mixtures of diaxial and diequatorial dibromo adducts in ratios depending on the substituent. 3-Benzoyloxy-substituted substrates gave, in addition, cis 1,2- and cis 1,3-dibromides. Only diaxial and diequatorial dibromo adducts, with a large prevalence (70–90%) of the former, were always obtained in all tribromide reactions. The kinetic and product results are consistent with an addition mechanism of molecular Br_2 involving a rate-determining ionization of olefin–Br_2 charge-transfer complexes (CTC's) to bromonium–tribromide ion pairs, followed by fast collapse to dibromo adducts. For the tribromide reactions they suggest instead a rate- and product-determining nucleophilic attack by bromide on olefin–Br_2 CTC's in equilibrium with the olefin and tribromide ions.

The use of organic tribromide salts in low polarity aprotic solvents as brominating reagents for conjugated carbon–carbon double bonds always gives more stereoselective anti 1,2-addition relative to molecular bromine.[1] This difference has been attributed to a change in the addition mechanism, and kinetic evidence for this has been produced in a recent investigation of the bromination of cyclohexene.[2] Of course, no difference in product could be observed with this substrate, *trans*-1,2-dibromocyclohexane being the only product.

Previous investigations had, however, shown[3] that in the case of allylically substituted cyclohexenes both diaxial and diequatorial adducts are obtained and that the product

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