in 4 mL of 1:1 $CS_2/CDCl_3$ and ^1H NMR spectral data were recorded at low temperature for **4**-d_2: ^1H NMR (1:1 $CS_2/CDCl_3$, −60 °C) δ 7.45–6.90 (m, 4 H), 5.58 (s, 1 H), 5.55 (s, 1 H). Upon warming to room temperature, 90% of **4**-d_2 was converted to **12**-d_4 and **13**-d_4 in a ratio of 4.4 to 1. After separation of **12**-d_4 and **13**-d_4 by TLC (silica gel plate, 5% ether in hexanes), their ^1H NMR spectral data were recorded. **12**-d_4: ^1H NMR ($CDCl_3$) δ 7.50–6.85 (m, 8 H), 2.94–2.80 (m, 2 H), 2.12–1.97 (m, 2 H). **13**-d_4: ^1H NMR ($CDCl_3$) δ 7.35–7.10 (m, 8 H), 3.15 (s, 4 H).

Diels–Alder Reaction of 4 with Methyl Acrylate. A 210-mg (0.789 mmol) quantity of (2-methyl-3-benzofuryl)methyl benzoate (**7**) was pyrolyzed at 630 °C. The pyrolysate was collected in 10 mL of a 1:1 mixture of methyl acrylate in CS_2 at −78 °C. The product was then slowly warmed to room temperature, dried (Na_2CO_3), and concentrated. TLC (silica gel plate, 5% ether in hexanes) yielded 64 mg (0.276 mmol, 35%) of 141.00 (12.14), 128.02 (10.57), 115.04 (29.67).

Diels–Alder Reactions of 4-d_2 with Methyl Acrylate. A 150-mg (0.557 mmol) quantity of [2-(trideuteriomethyl)-3-benzofuryl]methyl benzoate (**7**-d_3) was pyrolyzed at 630 °C. The pyrolysate was collected in 10 mL of 1:1 mixture of methyl acrylate in CS_2 at −78 °C. The product was then slowly warmed to room temperature, dried, and concentrated. TLC (silica gel plate, 5% ether in hexanes) yielded 51.7 mg (0.223 mmol, 40%) of the Diels–Alder adducts (**14**-d_2 and **15**-d_2): ^1H NMR ($CDCl_3$) δ 7.45–7.16 (m, 4 H), 3.75 (s, 3 H), 3.15–1.90 (m, 5 H); ^1H NMR (benzene-d_6) δ 7.42–7.12 (m, 4 H), 3.37 (s, 3 H), 3.33 (s, 3 H), 2.85–1.65 (m, 5 H).

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, under Contract W-7405-Eng-82.

Registry No. **4**, 98115-18-5; **4**-d_2, 103981-45-9; **7**, 98115-19-6; **7**-d_3, 103981-42-6; **8**, 26537-68-8; **9**, 3265-74-5; **9**-d_3, 103981-40-4; **10**, 53839-34-2; **10**-d_3, 103981-41-5; **11**, 131-76-0; **12**, 103981-43-7; **12**-d_4, 103981-46-0; **13**, 103981-44-8; **13**-d_4, 103981-47-1; **14**, 103981-48-2; **14**-d_2, 103981-50-6; **15**, 103981-49-3; **15**-d_2, 103981-51-7; $H_2C{=}CHCO_2CH_3$, 96-33-3.

Alkylation and Oligomerization of the Lithium Enolate of 2-Norbornenones. Stereochemical Consequences of Enolate Aggregation

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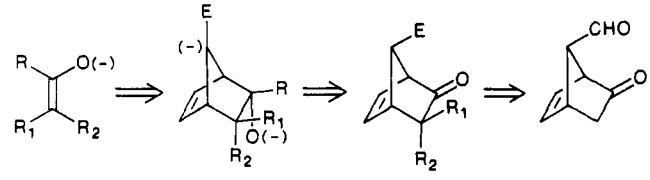
Alkylation of the lithium enolate of norbornenone in THF with alkyl halides gave a single trimeric oligomer containing one alkyl group as the major product. The structure of this diastereomer has been determined by ^1H and ^{13}C 2-D NMR techniques and analysis of relaxation times. Direct reaction in the aggregated enolate with the Zimmerman–House–Jackman cubic structure is implied. Compounds with a 7-anti substituent could be alkylated in satisfactory yield. The use of the dimethylhydrazone anion as an enolate equivalent gave good yields of 3-alkylnorbornenones (methyl, *n*-hexyl, benzyl). ^1H and ^{13}C NMR data for products and intermediates are reported.

The combination of the convenient industrial scale synthesis of 7-substituted norbornenones[1] with the anion-induced retro-Diels–Alder reaction[2] to generate specifically substituted enolates and olefins appeared attractive (Scheme I). In the course of this endeavor,[3] the alkylation of the lithium enolate of 2-norbornenone (II) was undertaken and a unique trimeric product (V) obtained under standard reaction conditions. A hypothesis is proposed for the preferential formation of trimer and the preference for only one of its 128 possible isomeric forms. Formation of V is postulated to occur through the Zimmerman–House–Jackman cubic structure for aggregated lithium enolates.[4] This contrasts with the enolate of 2-norbornanone which undergoes alkylation in good yield.[5] A practical alkylation of norbornenone is accomplished through the hydrazone methodology.[6] The synthetic results are presented first. The detailed nmr experiments necessary to establish the unique structure V is next. The discussion of how V is formed follows and then the Experimental Section. A compilation of ^{13}C shifts of substituted norbornanes is presented as supplementary material.

Scheme I



Results

Enolate Preparation and Alkylation. The lithium enolate of 2-norbornenone (II) was prepared by the addition of the ketone to lithium diisopropylamide (LDA) in THF. Quenching with propionaldehyde gave III as a single isomer in 84% isolated yield. This confirms that enolate II is stable and readily prepared in good yield.

Treatment of II with a series of alkyl halides gave poor yields of the anticipated 3-alkylnorbornenone (IV) (Table

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(6) (a) Stork, G. L.; Benaim, J. *J. Am. Chem. Soc.* **1971**, *93*, 5938. (b) For a review see: Enders, D. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3, Chapter 4.

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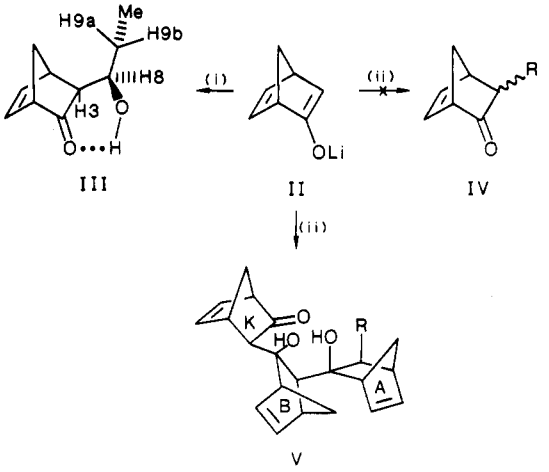
Table I. Reaction of the Lithium Enolate[a] and Dimethylhydrazone Anion[b] of Norbornenone with Alkyl Halides in THF

RX[c]	enolate/hydrazone[d]	time,[e] h	% yield product[f] IV_x[g]	IV_n	V	other[h]
MeI	II	*i*	20			4[j]
MeI	II-D	0.16	(94)			
MeI	*anti*-II	*i*	25	58		10[k]
HxI	II	18	2.5		*m*	5[l]
HxI	II	3	*m*		8	
HxI	II-D	0.25	66 (87)			
HxI	*anti*-II	50		35		
HxI	*syn*-II-D	3	45 (70)			
HxI	VII[n]	*i*	73			
AlBr	II	0.5	*m*		48	
AlBr	II	4[o]	30	10	*m*	
BzCl	II	3	*m*		13	
BzCl	II-D	0.5	70 (85)			

[a] Scheme II. [b] Scheme III. [c] Identifies R group in alkylating agent and products IV and V, Me = methyl (**a**), Hx = *n*-hexyl (**b**), Al = allyl (**c**), Bz = benzyl (**d**). Stereochemical details in V not specified. [d] See Schemes II and III for structures. [e] Time after addition, allowed for solution to warm to room temperature. Reactions with times greater than 4 h were preliminary runs and are included for information only. [f] Isolated yields after purification. [g] Yields in parentheses are alkylated hydrazone VI-D isolated prior to hydrolysis. [h] Crude yield of unpurified product. [i] Overnight (~16 h). [j] Dimer from Ia with II. [k] Dimer from *anti*-Ia with *anti*-II. [l] Dimer from I with II. [m] <5% of this material identified in product mixture but not isolated. [n] VII is 2-norbornanone enolate. [o] At reflux.

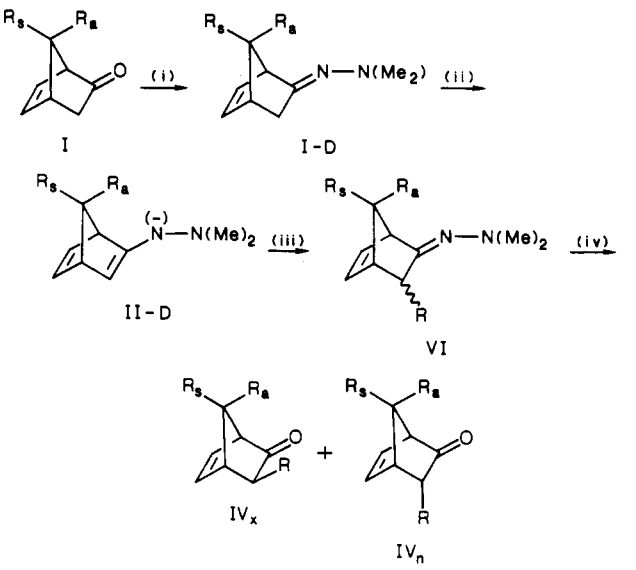
Scheme II[a]



[a] R = methyl (**a**), hexyl (**b**), allyl (**c**), benzyl (**d**). (i) propionaldehyde, −78 °C, 5 min; (ii) alkyl halide, −78 °C, then warm to room temperature (see Table I), NH_4Cl.

I) (20% for methyl and less than 5% for other alkyls). When allyl bromide was reacted with II for a few minutes, a 48% yield of monoalkylated trimer Vc was isolated after flash chromatography. The TLC of the reaction mixture prior to chromatography showed at least six different products. The complexity of the reaction mixture increased with time, and the yield of Vc diminished. On workup, small amounts of monoalkylated monomer IVc, trimer Vc, and dimer were isolated. The remaining material was inferred to be a mixture of higher oligomers and stereoisomers from its TLC mobility. The yield of 3-allylnorbornenone, IVc, could be increased to 40% (3:1 exo/endo) by using a large excess of allyl bromide and increasing the reaction time. Extensive reversible oligomerization is indicated and is responsible for the reduced yield of alkylated product. Literature reports[7,8] that the enolate of norbornanone—the saturated analogue—could be alkylated in good yield were confirmed. The contrast with norbornenone alkylation is noted.

Scheme III[a]



	R_s	R_a	R
IVa	H	H	Me
b	H	H	C_6H_{13}
c	H	H	$CH_2C_2H_3$
d	H	H	$CH_2C_6H_5$
anti-I	H	$CH(OMe)_2$	
syn-I	$CH(OMe)_2$	H	

[a] (i) dimethylhydrazine; (ii) LDA/THF, 0 °C; (iii) R–X, −70 to −50 °C, THF; (iv) aqueous HCl, 0 °C.

Intriguingly, but consistent with literature observations,[9] simple alkylation becomes the predominant reaction when an *anti*-dimethoxymethyl substituent is present at C-7. The exo face of the enolate is blocked, and the endo methyl- and hexylalkylates are isolated in satisfactory yield—IVa-n, 58%, and IVb-n, 35%, respectively.

Hydrazone Alkylation (Scheme III). The dimethylhydrazone anion is a useful alternative to the eno-

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(8) Reference 5a, pp 21–29.

(9) (a) Grieco, P. A.; Takigawa, T.; Moore, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 4380–1. (b) Grieco, P. A.; Majetich, G. F.; Ohfune, Y. *J. Am. Chem. Soc.* **1982**, *104*, 4226–4233. (c) Grieco, P. A.; Inanaga, J.; Lin, N.-H.; Yanami, T. *Ibid.* **1982**, *104*, 5781–4. (d) Grieco, P. A.; Ohfune, Y. *J. Org. Chem.* **1980**, *45*, 2251–4. (e) Trost, B. M.; Bernstein, R. R.; Funfschilling, P. C. *J. Am. Chem. Soc.* **1979**, *101*, 4378–80.

Table II. NMR Data for Trimer Vc

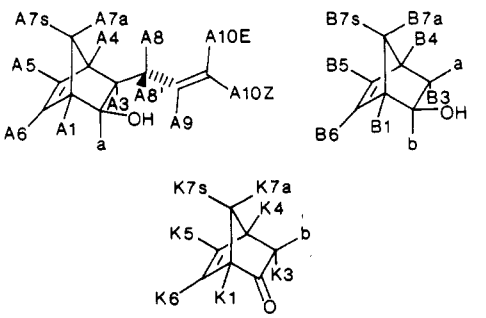
proton/ carbon assignt	proton chem shift, ppm	coupling const,[a] Hz	proton T_1,[b] s	carbon chem shift,[c] ppm
K5	6.69	5.60 (K6), 2.95 (K4), 1.0 (K1), (K7a)[d]	1.45 (1.52)	145.10
B5	6.30	5.74 (B6), 3.35 (B4), (B1),[d] (B7a)[d]	1.53 (1.62)	142.04
K6	6.23	5.60 (K5), 3.18 (K1), 0.8 (K4), 0.8 (K7a)	1.84 (1.96)	133.26
A5	6.19	5.81 (A6), 3.11 (A4), 0.7 (A1), (A7a)	1.53 (1.58)	139.61
B6	5.99	5.74 (B5), 2.82 (B1), 0.88 (B7a), 0.7 (B4)	1.06 (1.10)	133.71
A9	5.90	17.12 (A10*Z*), 10.07 (A10*E*), 7.85 (A8), 6.03 (A8′)	1.57 (1.69)	139.20
A6	5.75	5.81 (A5), 3.06 (A1), (A4), (A7a)	0.98 (0.98)	134.05
A OH	5.70		1.00	
A10*Z*	5.06	17.12 (A9), 2.25 (A10*E*), 1.80 (A8′), 1.18 (A8)	1.35 (1.39)	114.97
A10*E*	5.00	10.07 (A9), 2.25 (A10*Z*), 1.41 (A8′), 0.99 (A8)	1.41 (1.42)	114.97
B OH	4.40		1.00	
K1	3.04	3.18 (K6), 1.80 (K7a), 1.60 (K4), 1.40 (K7s), (K5)	1.75 (1.91)	55.53
K4	2.96	2.95 (K5), 2.30 (K7s), 1.60 (K1), 1.6 (K7a), 0.8 (K6)	0.85 (0.90)	43.08
A1	2.89	3.06 (A6), 1.80 (A7a), 1.8 (A7s), 1.7 (A4), 0.7 (A5)	0.86 (1.10)	55.14
B4	2.68	3.35 (B5), 1.76 (B7s), 1.75 (B7a), 1.8 (B1), 0.7 (B6)	0.76 (0.80)	44.69
A4	2.59	(A7a),[e] (A7s),[e] (A1)[e]	0.95[g] (1.04)	44.76
B1	2.59	(B7a),[e] (B7s,[e] (B4)[e]		52.03
A8′	2.55	14.9 (A8), 6.03 (A9), 0.0 (A3), 1.80 (A10*Z*), 1.41 (A10*E*)		34.98
K3	2.52	3.94 (K7s)	0.72 (0.78)	52.55
B7a	2.31	8.54 (B7s), 1.75 (B1), 1.70 (B4)	0.43[g] (0.48)	48.94
K7a	2.29	9.70 (K7s), 1.80 (K1), 1.60 (K4), (K6)	0.43[g] (0.48)	49.24
K7s	2.14	9.70 (K7a), 3.94 (K3), 2.30 (K4), 1.40 (K1)		49.24
A7a	2.06	8.49 (A7s), 1.80 (A1), 1.80 (A4)	0.47 (0.48)	45.64
A8	1.95	14.9 (A8′), 11.38 (A3), 7.85 (A9), 1.18 (A10*Z*), 0.99 (A10*E*)	0.54 (0.53)	34.98
B7s	1.54	8.54 (B7a), 1.76 (B1), 1.75 (B3), 1.72 (B4)	0.58 (0.58)	48.94
B3	1.46	1.75 (B7s)		55.44
A7s	1.42	8.49 (A7a), 1.77 (A3), 1.76 (A4), 1.75 (A1)	0.65[g] (0.67)	45.64
A3	1.36	11.38 (A8), 3.0 (A8′), 1.77 (A7s)	0.68 (0.68)	47.89
A2				221.06
B2[f]				84.53
K2[f]				81.70

[a] The coupled proton is given in parentheses. Cross peaks in the homonuclear COSY experiment were detected in all cases except those underlined. [b] Values in parentheses for compound with OH exchanged to OD. [c] Connectivity confirmed for all protonated carbons by detection of a cross peak in the heteronuclear COSY experiment. [d] An unresolved coupling of <1 Hz was present. [e] Protons not resolved ($\Delta\delta$ < 1 Hz). Couplings determined from coupled protons and line width. [f] Assignments may be reversed. [g] Net T_1 for overlapped proton group.

late in alkylation reactions.[6] The dimethylhydrazone of 2-norbornenone was prepared by direct reaction with dimethylhydrazine, deprotonated with LDA in THF at 0 °C, alkylated at −50 to −70 °C in good yield, and then hydrolyzed to the desired alkyl ketone IV in satisfactory yield. Norbornenone, s-I, with a *syn*-7-dimethoxymethyl group is alkylated similarly in comparable yield (Table I).

NMR Structure Determination—Stereochemistry of III. The location of substituents on the norbornenyl framework is accomplished from the characteristic coupling patterns.[10] III exists in an intramolecularly hydrogen-bonded conformation in $CDCl_3$ (J_{34} < 1 Hz; J_{38} = 9.6 Hz; J_{89a} = 0 Hz; J_{89b} = 3 Hz). This is confirmed in Me_2SO (J_{34} < 1 Hz; J_{38} = 4.8 Hz; J_{89a} = 4.3 Hz; J_{89b} = 8.1 Hz) where the intramolecular hydrogen bond is lost and the side chain couplings reflect the rotational freedom between conformers. The small value of J_{34} places the substituent in the exo orientation at C-3. In $CDCl_3$, the hydrogen bonding holds H-3 and H-8 in the same plane. The small couplings between the carbinol proton H-8 and the methylene protons show that the three-carbon side chain exists in a restricted conformation. One of the methylene protons has a 90° dihedral angle with respect to H-8 and the other has a typical gauche value. Models of the diastereomers which differ in configuration at C-8 show that the 3*S*,8*R* structure is the only one consistent with the data assuming the hydrogen bonded form. [Racemic starting materials were used throughout this work. Chiral products are racemic mixtures, and *R*–*S* terminology is used to designate relative stereochemistry.] If H-3 and H-8 are anti-periplanar, the ethyl group is pointed away from the rest of the frame work and should be freely rotating. In the eclipsed arrangement of H-3 and H-8, the ethyl group is confined in proximity to C-7 and the methyl group is forced away from the ring and rotation about C8–C9 is heavily restricted. In the alternative diastereomer, intramolecular hydrogen bonding and coplanar H-3 and H-8 are mutually incompatible.

Structure of Trimer Vc. The formula $C_{24}H_{28}O_3$ was established by mass spectrometry and combustion analysis. The 24 carbon peaks and 27 resolved proton resonances (two bridgehead protons absorb together) showed Vc to be a single diastereomer comprised of three norbornenyl units and one allyl substituent. The characteristic norbornenyl chemical shifts and coupling patterns[10] were analyzed from resolution enhanced spectra, and the details are given in Table II.



Homonuclear proton COSY spectra connected the protons to the three norbornenyl units A, B, and K. The endo orientation of H-3 of each ring was established by the absence of coupling with H-4 and the sizable coupling with H-7 syn. The two sharp (line width < 1 Hz) singlets for

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the hydroxyl protons at δ 5.70 and 4.40 indicate significant hydrogen bonding. There is slow exchange (>0.1 s^{-1}) between them and with adventitious water. D_2O exchange was also slow (~15 min). The magnitude of the coupling between H-3 and the allylic protons in ring A shows that the allyl group exists predominantly in a single conformer with protons A8 and A3 lying in the same plane. The stereochemistry at C-2 in B and K and the connectivity of the C-2–C-3 unit to the norbornyl frame in all three rings require more than a proton spectrum for assignment.

The olefinic proton and carbon assignments for the keto ring K were based on the chemical shifts of norbornenones[11] and confirmed by homonuclear (^1H–^1H) and heteronuclear (^1H–^{13}C) COSY[12] cross peaks. Heteronuclear COSY also identified C-1 and C-4 in the carbon spectrum. The high-frequency resonances (55.14, 52.03, and 55.53 ppm) were assigned to C-1 and the low frequencies (44.76, 44.69, and 43.08 ppm) to C-4 in A, B, and K, respectively. C-1 is adjacent to a quaternary center whereas C-4 is adjacent to a tertiary. All protons and carbons, except the hydroxyl protons and C-2, are now uniquely identified and linked to their coupled neighbors. The stereochemistry of the hydroxyl groups was established by differential proton T_1 measurements.[13] Exchange of deuterium for hydrogen produced a 10% or larger increase in T_1 at positions A1, B7a, K1, K3, and K7a. This requires that the hydroxyl protons are within 1.5 times the distance to other proton neighbors at these positions. These constraints are only met if both hydroxyl groups are exo and are nicely consistent with two intramolecular hydrogen bonds.

The selection of the correct diastereomer from the four remaining possible structures—(*R*)-A (*R*)-B (*R*)-K, (*R*)-A (*R*)-B (*S*)-K, (*R*)-A (*S*)-B (*R*)-K, and (*R*)-A (*S*)-B (*S*)-K—was made from proton T_1 and NOE data. Intramolecular dipole–dipole relaxation is the only mechanism sufficiently rapid and sufficiently selective to account for the magnitude and variation of T_1 shown in Table II.[13] To start the analysis, it was assumed that the trimer was tumbling isotropically and existed predominantly in a single conformation. The results are consistent with these assumptions—see below. Under these assumptions, the relaxation time (T_{1i}, s) of proton i is determined by the interproton distances (r_{ij}, Å) as given by

$$1/T_{1i} = K\sum_{j\neq 1}(1/r_{ij}^6) \qquad (1)$$

K is a constant

In the absence of interaction between rings all olefinic protons would have the same T_1 values as the geometry of the framework is fixed. The bridgeheads and bridge protons should also give a common value for each group. The data in Table II show that this is not the case. For example, the T_1 for A6 is half that for K6 and A1 has half the K1 value. The A1–A6 distance would need to be 0.3 Å shorter than the K1–K6 distance to explain the difference. The maximum distortion observed in an X-ray study[1] of norbornenyl compounds was ±0.01 Å in the bond lengths and ±1° in the bond angles. Further, the T_1 variation cannot be attributed to anisotropic reorientation of H–H dipoles. In the norbornenyl skeleton, the dipole vectors between neighboring protons cover the full range of spatial orientations. Thus the effects of anisotropic motion could not be localized to a particular internuclear vector. As there is no correlation between proton–proton vector direction cosines and T_1 times, the dipolar reorientation must be essentially isotropic. This is consistent with the approximately spherical structure of V in any of its conformations. If the protons with short relaxation times (A6, B6, A1, B1, F4, K4) and those with long relaxation times (A5, B5, K6, K1) are grouped, a rational involving inter-ring cross relaxation is suggested. This is placed on a rational basis by comparing the relaxation of the protons at C-7 (~0.5 s) with the olefinic protons. On the basis of their internuclear separations, the olefinic protons would be predicted to have a relaxation time of ~2.5 s consistent with the slow relaxing group. The faster relaxing protons must then be on the inside of the molecule. They must be as close or closer to protons in other rings as they are to those on the same ring.

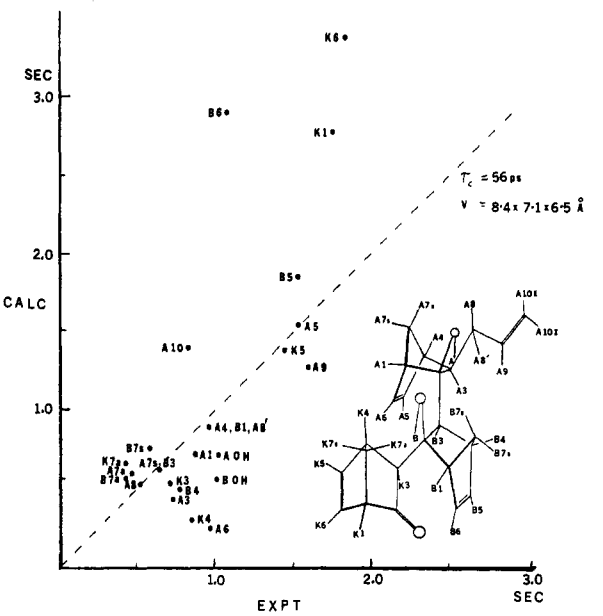

Figure 1. The proton T_1 relaxation times for each proton of trimer V (~1 M) in $CDCl_3$. Comparison of experimental values with those calculated for optimized rotamer using eq 1 Dashed line; τ_c is correlation time calculated for a compound of volume 388 $Å^3$.

The dependence of T_1 on inter-ring contact provides a basis for distinguishing diastereomers. A computer model of the four diastereomers was constructed by using the norbornenyl coordinates of Simonetta et al.[15] and standard bond lengths[16] for substituents. Rotation in 30° steps about the two inter-ring bonds were performed and interproton distances calculated at each step. Structures with several interproton distances less than 1.7 Å were rejected. The observation of a 14% NOE between A6 and K5 was used to reduce the possible conformers from 36 to 2. Both A6 and K5 have two neighboring protons on the same ring within 2.6 Å. For a 14% NOE, between A6 and K5 the spatial separation between them cannot be greater than 3 Å for inter-ring relaxation to be competitive

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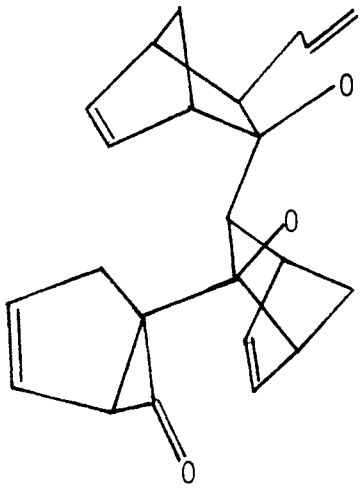

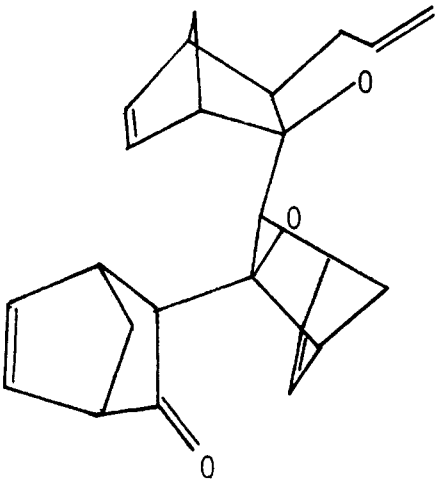

Figure 2. Stereo representation of trimer Vc.

with intra-ring contributions. The two conformers selected on this basis had the (*R*)-A (*S*)-B (*R*)-K structure. The final structure was selected on the basis of the best agreement between observed and calculated T_1 (Figure 1). The correlation is remarkably good considering the assumptions of isotropic tumbling, standard geometries, pure dipolar relaxation, and the great sensitivity of the R^{-6} dependence to molecular distortion. Proton pairs in closest contact, A3 and B4 and A6 and K4, give the poorest correlation, but they are also the most sensitive to minor distortions. All four would show at least a factor of 2 larger errors if the structure were varied by a 5° rotation around the inter-ring bonds. Protons K1, K6 and B6 show deviations because the X-ray determination of proton position is imprecise. The X-ray data give a H-1–H-6 separation of 3.05 Å whereas the H-4–H-5 separation is 2.42 Å. This latter value is close to that predicted from Dreiding models. Reduction of the H-1–H-6 separation from 3.05 to 2.5 Å would reduce the calculated values to 2.52 s for K6 and 2.17 s for K1 and bring these protons close to the correlation line.

Greater refinement seemed unnecessary considering the overall agreement and the level of computation necessary to achieve a closer match. It was gratifying to note that the structure had an oxygen configuration appropriate for hydrogen bonding since this information had not been used in the T_1 analysis. Further the hydroxyl T_1 values—both 1 s—and the change at other positions when hydrogen is replaced by deuterium show that these protons relax each other. A hydroxyl–hydroxyl interproton distance of 1.9 Å was determined from T_1 and compares well with the 2.2-Å distance determined from the model derived structure.

The straight line in Figure 1 was calculated from the theory of rotational relaxation employing a modified Stokes–Einstein model for the evaluation of K.[17] According to theory, $K = {}^3/_2\gamma^4\tau_c$ where γ is the proton gyromagnetic ratio and τ_c is the rotational correlation time. τ_c was estimated from the molecular dimensions with $\tau_c = f_{GW}V\eta/T = 56$ ps. The volume V (Å^3) was calculated from the product of the maximum dimensions of the molecular model (8.4 × 7.1 × 6.5 Å^3). The viscosity (η = 0.56 cP) was the value for pure chloroform, and f_{GW} is an empirical factor[17-19] required to correct the Stokes–Einstein

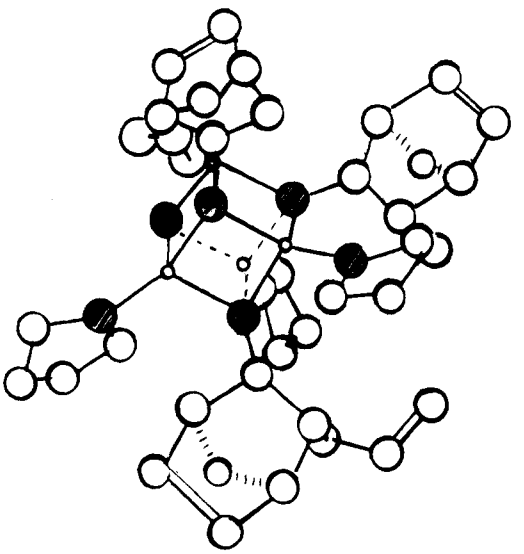

Figure 3. Proposed ZHJ tetrameric transition state for the (X^-, *R*, *S*, *R*) enolate complex.

model when the solute and solvent are of comparable size (f_{GW} = 0.257). The quantitative agreement with the results is almost too good to be true.

The refined structure of trimer Vc in its preferred conformation is shown in Figure 2.

Discussion

It is premature to reach concrete mechanistic conclusions from this study as tests for reversibility of enolate addition and for base-catalyzed epimerization were not made. Our mechanistic analysis was strictly ad hoc. A mechanism is proposed, however, because it rationalizes the contra-entropic results and accounts for the observations within a single working hypothesis. The tetrameric cubic structure of enolates in THF was proposed by House[20] and established in solution by Jackman and Szevereny[19] and in the solid state by Dunitz et al.[21] Since the pioneering work of Bartlett,[22] evidence for reactions

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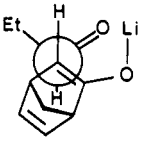
occurring in tetrameric lithium species has grown.[23,24] The stereochemical consequences of the cyclic Zimmerman[25]–House–Jackman (ZHJ) transition state for enolate addition to carbonyl has been elaborated recently.[5a,7,26] The combination of these ideas provides the rationale for our results.

The Unique Structure V. Norbornenone forms a racemic mixture of (*E*)-enolates. Two enantiomeric pairs plus a "meso" form of tetrameric diastereomers may be formed in principle (*RRRR*, *SSSS*; *SRRR*, *RSSS*, *SSRR*).[26] Replacement of one enolate by halide (X) at one cubic site in the process of alkylation[23] and generation of a keto site by exo alkylation[5a] gives four possible pairs of enantiomeric complexes (X*RRR'*; X*RSR'*; X*SRR'*; X*SSR'*). Packing considerations favor the X*RSR'* geometry. As reflected in the hydrogen-bonded product V, this ketone–enolate–enolate–halide tetramer is held in just the geometry necessary for oligomerization to form V. It meets the constraints of the ZHJ transition state. The alkyl ketone must react on the endo face and the enolates on the exo face according to models. The *RSR'* combination is the only one which will permit trimerization. The *SSR'* is the second best model. The dichotomy between norbornenone and norbornanone alkylation is rationalized in the same manner. The presence of the endo hydrogens in the saturated enolate greatly destabilizes the ZHJ geometry in the tetramer, and it is unable to form. Similarly the presence of seven substituents prevents formation of the required complex. Presumably alkylation takes place in lower aggregates for these substrates (e.g., monomer or tetramer containing a single enolate), and oligomerization does not occur. Cristol and Freeman[27a] and Gassman[27b] have previously noted the dimerization of norbornenone and its enolate. An intriguing prediction of this analysis is that resolved norbornenone should give the simple alkylated monomer IV in the same manner as norbornanone under standard enolate conditions. The tetramer composed of norbornenone enolates of the same chirality is too sterically crowded to exist and so simple alkylation should occur.

The Stereochemistry of III. The intramolecular hydrogen bonding observed in the product III provides a significant clue to the nature of the enolate transition state. The geometric requirements for hydrogen bonding in the product correspond to the geometric requirements for the ZHJ transition state. The rigidity of the norbornyl framework limits the conformational possibilities, and the methylene protons adjacent to the carbinol center report the conformational preference of the substituent. For example, in III, the coupling between the carbinol methine proton H-8 and the methylene protons H-9 shows that the ethyl substituent exists predominantly in a single conformation in $CDCl_3$. When the hydrogen bonding constraint is lifted, the ethyl group becomes free to rotate.

The enolate transition-state complex will be subject to the same steric constraints observed in the hydrogen-bonded product. To generate the sterically congested product III there must be some key constraints on propionaldehyde in the ZHJ transition-state complex. Consideration of the optimum complex formed on the exo face of the (*E*)-norbornenone enolate (cf. ref 7, p 155) shows no evidence of steric constraint on ethyl rotation, and the opposite diastereomer is predicted. In the chair form of the complex, however, the aldehyde proton collides with the 7-anti proton and this may be responsible for the absence of this product. Either the ZHJ transition state is more ramified (e.g., dimer or trimer) to introduce additional steric interactions, or, the rationale we prefer, the observed exo product is the result of epimerization during the quench. With the alternative assumption that condensation is preferred on the endo face of II, the stereochemistry is rationalized. The ZHJ transition state for condensation with propionaldehyde is shown (cf. ref 7, p 155) and is free of steric interaction. Subsequent epimerization gives III.



Carbon-13 NMR. In the course of these studies, a variety of substituted norbornenones have been prepared and ^{13}C NMR spectra obtained. Compounds substituted at the 7-position with carboxylic acid, ester, carboxaldehyde, and its dimethyl acetal in syn and anti orientations are available. Their preparations follow the methods described here[3] and in the literature.[1] ^{13}C spectral data are recorded as supplementary material for reference purposes.

Conclusions

1. A specific aggregated enolate complex has been proposed to account for the formation of V as the unique major product of the alkylation of norbornenone.
2. The formation of a single product out of 128 possible enantiomeric pairs of trimers demonstrates the specificity obtainable from aggregation of enantiomers into diastereomeric complexes.
3. The contrast between alkylation of norbornenone and its substituted derivatives and norbornanone highlights the subtleties of stereolectronic control in complex aggregates.
4. The proposal is testable by the alkylation of resolved norbornenone enolate.
5. Reaction in an aggregate is expected to occur widely, but rapid retro-aldol reaction and further polymerization have inhibited detection.
6. The Corey–Enders hydrazone methodology is the preferred method for alkylation of norbornanones.
7. The use of aldehydes of the form RCH_2CHO is recommended as probe for the structure of the enolate–carbonyl transition state.

Note Added in Proof. A single-crystal X-ray structure determination of trimer Vc is in progress. The preliminary structure confirms the structure determined by NMR. Full details will be published after the refinement.

Experimental Section

^1H NMR spectra (90 MHz, Perkin-Elmer R-32; 200 MHz, Varian XL-200) and ^{13}C NMR (20 MHz, Varian CFT-20; 50 MHz, Varian XL-200) were obtained in $CDCl_3$ with chemical shifts in parts per million to high frequency from internal Me_4Si unless noted otherwise. The symbol $\{x\}_y$ denotes that the coupling constant x (Hz) to the proton at $\delta = y$ (ppm) was confirmed by double resonance. APT spectra gave an even (e) or odd (o) proton count for each carbon. Mass spectra (Finnigan 4000) were obtained by direct ionization (70 eV) or chemical ionization (isobutane). IR spectra (cm^{-1}) (Perkin-Elmer 267 or 710B) were

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obtained as films for liquids and KBr pellets or Nujol mulls for solids. Uncorrected boiling points and melting points are reported. Microanalysis was performed by the Purdue University microanalytical facility.

Flash column chromatography (FCC)[28] was performed by using 230–400 mesh silica gel (EM reagents) with the specified pentane:ether (P:E) ratio as eluant. TLC was performed with precoated silica gel 60 F-254 plates (0.25 mm) and visualized in an iodine chamber.

Reactions were run under a positive pressure of nitrogen with oven-dried glassware (140 °C, ≥3 h). Reagents were introduced via syringe through rubber septa. Reactions were typically worked up by pouring into water and extracting with an organic solvent (Et_2O, pentane, hexane, methylene chloride, or chloroform). The organic layer was dried over anhydrous magnesium sulfate and the solvent removed on a Büchi rotovapor at aspirator pressure.

Reactions run at −78 °C were cooled in a dry ice–2-propanol slush bath. Reactions run at −10 to 0 °C were cooled by using a sodium chloride and ice slush bath.

Reagents were commercial materials used without additional purification unless specified otherwise. Tetrahydrofuran (THF), Fisher reagent grade, was predried over sodium ribbon, distilled from sodium benzophenone ketyl under nitrogen in a reflux still, and transferred by syringe. Diisopropylamine was distilled from calcium hydride prior to use. *n*-Butyllithium (1.8–2.5 M in hexane) was titrated[29] prior to use.

Enolate Solutions and Alkylation Procedure A. Lithium Bicyclo[2.2.1]hepta-2,5-diene 2-Oxide (II). Diisopropylamine (1.5 mL, 10 mequiv) was dissolved in THF (20 mL) and cooled to −78 °C. *n*-Butyllithium (10 mequiv) was added and the mixture warmed to room temperature for 15–30 min. This LDA solution was recooled to −78 °C. Norbornenone (I; 1 g, 9.4 mequiv) in THF (30 mL) was added dropwise over 1 h to form II. The alkyl halide was then added and the solution allowed to warm to room temperature and stirred for various periods of time. Reaction mixture was poured into water and neutralized and ether extracted. TLC examination and FCC isolation followed.

Preparation of Bicyclo[2.2.1]hept-5-en-2-one Dimethylhydrazone (I-D). Bicyclo[2.2.1]hept-5-en-2-one (10.0 g, 0.092 mol) and 1,1-dimethylhydrazine (6.0 g, 0.1 mol) were heated to 70 °C for 1 h. The reaction was poured into water, extracted with CH_2Cl_2, dried, and rotovaped. The crude product was vacuum distilled (bp 60–70 °C at 0.5 mm) to give the dimethylhydrazone I-D (12.2 g, 88% yield) as a 3:1 mixture of *E* and *Z* isomers, respectively. Stereochemistry was based on the assumption of a syn upfield shift at the α-carbon. ^{1}H NMR: δ 6.35 (m, 1 H, H-5), 6.10 (m, 1 H, H-6), 3.90 (m, 0.3 H, H-1_Z/H-4_Z), 3.25–3.05 (m, 1.7 H, H-1 and H-4 plus H-1_z/H-4_z), 2.47 and 2.44 (s, 1:3 ratio, 6 H, NMe_2 and NMe_{2z} respectively). 2.30–1.50 (m, 4 H). ^{13}C NMR: δ 173.69 (e, C-2), 140.60 (o, C-5_Z), 139.78 (o, C-5), 132.94 (o, C-6), 131.95 (o, C-6_Z), 50.44 (o, C-1), 50.35 (e, C-7), 49.92 (e, C-7_Z), 48.28 (o, C-1_Z), 47.15 (NMe_2), 46.44 (o, NMe_{2Z}), 40.97 (o, C-4), 40.00 (o, C-4_Z), 34.07 (e, C-3_Z), 32.49 (e, C-3).

Dimethylhydrazone Anion II-D and Alkylation Procedure B. Dimethylhydrazone I-D (7.5 g, 0.05 mol) in THF (20 mL) was added dropwise to an LDA solution (50 mequiv, see above) at 0 °C and stirred for 1 h. A precipitate of hydrazone anion II-D forms as addition proceeds. The suspension of II-D was cooled to −50 to −40 °C, and alkyl halide (0.06–0.07 mol) in THF (20 mL) was added dropwise. The addition rate was adjusted to maintain the exothermic reaction below −40 °C. Water quench, ether extraction, drying, rotary evaporation, and vacuum distillation or FCC (4:1, P/E) completed the workup of alkylated hydrazone VI. Hydrolysis of VI was accomplished on a 0.02-mol scale in a solution of aqueous 2.5% HCl (50 mL) in THF (50 mL). Reaction was followed by TLC until VI had been consumed (<1 h) and worked up in the same manner as VI above and the alkylated ketone IV isolated.

***exo*-3-(1-Hydroxypropyl)bicyclo[2.2.1]hept-5-en-2-one (III).** Propanal (0.7 g, 0.012 mol) in THF (5 mL) was added rapidly (5 s) to the enolate solution (II, 0.01 mol, 30 mL) at −78 °C. The reaction was checked immediately by TLC and found to be complete. The reaction was worked up by pouring into NH_4Cl (aqueous saturated solution), extracting with ether, drying, and rotovaping to give crude product III (1.56 g). FCC (3:1, P/E) gave III (1.4 g, 84%). ^{1}H NMR: δ 6.65 (dd, *J* = 5.6, 2.9 Hz, 1 H, H-5), 6.19 (dd, *J* = 5, 3.2 Hz, 1 H, H-6), 3.55 (m, 2 H, H-8, OH), 3.06 (m, 1 H, H-1/H-4), 3.00 (m, 1 H, H-1/H-4), 2.20 (d, *J* = 9.6 Hz, 1 H, H-7 anti), 2.10 (bdd, *J* = 9.6 Hz, $\{3.3\}_{1.8}$, 1 H, H-7 syn), 1.86 (dd, *J* = $\{9.6\}_{6.6}$, $\{3.3\}_{2.1}$, 1 H, H-3 endo), 1.65 (dqd *J* = 14, 7, 3 Hz, 1 H, H-9a), 1.47 (dq, *J* = 14, 7 Hz, 1 H, H-9b), 0.98 (t, *J* = 7.4 Hz, 3 H, Me). ^{1}H NMR (Me_2SO-d_6): δ 6.65 (dd, *J* = 5.5, 2.9 Hz, 1 H, H-5), 6.21 (dd, *J* = 5.6, 3.0 Hz, 1 H, H-6), 4.54 (d, *J* = $\{5.1\}_{3.5}$, 1 H, OH), 3.52 (apparent dq, *J* = $\{7\}_{1.6}$, 5 Hz, 1 H, H-8, J_{actual} = $\{8.1\}_{1.6}$, $\{5.1\}_{4.5}$, 4.8, 4.3 Hz), 2.98 (m, 1 H, H-1/H-4), 2.84 (m, 1 H, H-1/H-4), 2.50 (m, 1 H, H-7 anti), 1.89 (m, 1 H, H-7 syn), 1.80 (dd, *J* = 4.8, 3.3 Hz, 1 H, H-3 endo), 1.55 (m, 2 H, H-9a, H-9b, AB pattern J_{AX} = 4.3 Hz, J_{BX} = 8.1 Hz, J_{AB} = −13.6 Hz, δ_{AB} = 8.0 Hz, all quartet split *J* = 7.5 Hz), 0.85 (t, *J* = 7.5 Hz, 3 H, Me). ^{13}C NMR: δ 219.02 (s, C-2), 144.03 (d, C-5), 132.03 (d, C-6), 73.01 (d, C-8), 58.61 (d, C-1), 49.68 (d, C-3), 47.71 (t, C-7), 42.71 (d, C-4), 28.05 (t, C-9), 9.07 (q, Me).

***exo*-3-Methylbicyclo[2.2.1]hept-5-en-2-one Dimethylhydrazone (VIa-x). Procedure B.** Alkylation with methyl iodide was complete in 10 min at −40 to −50 °C and the hydrazone VIa-x obtained in 94% yield after vacuum distillation (bp 28–31 °C (0.7 mm) as a single isomer. ^{1}H NMR: δ 6.33 (dd, *J* = 5.5, 2.9 Hz, 1 H), 6.11 (dd, *J* = 5.6, 3.2 Hz, 1 H) 3.15 (m, 1 H) 2.65 (m, 1 H), 2.38 (s, 6 H, NMe_2), 2.35 (dq, *J* = 7.0, 2.4 Hz, 1 H, H-3 endo), 1.91 (d, *J* = 8.7 Hz, 1 H, H-7 anti), 1.70 (d, *J* = 8.7 Hz, 1 H, H-7 syn), 1.31 (d, *J* = 7.2 Hz, Me); $J_{3n-7syn}$ = 2.4 Hz, J_{3n-4} = 0 Hz. No resonances assignable to the endo isomer were observable. Mass spectrum (EI, 70 eV): *m/e* (intensity) 164 (M^+, 40), 149 (13), 120 (5), 98 (58), 93 (7), 83 (100), 77 (16), 66 (22), 55 (12), 45 (16), 44 (68), 43 (33), 42 (27). Hydrolysis of VIa-x to ketone was not performed.

***exo*-3-Methylbicyclo[2.2.1]hept-5-en-2-one (IVa-x) and the Corresponding Dimer. Procedure A.** Reaction was carried out on a 0.01-mol scale and gave IVa-x[11] in a 20% yield after overnight reaction followed by FCC (10:1 P/E). The aldol dimer from IIIa-x and I—stereochemistry not established—was obtained in 4% yield after FCC (4:1, P/E). Dimer: ^{1}H NMR δ 6.60 (dd, *J* = 6, 3 Hz, 1 H), 6.10 (m, 3 H), 3.20–2.80 (m, 5 H), 2.20 (m, 6 H), 1.10 (d, *J* = 7 Hz, 3 H); ^{13}C NMR δ 216.26 (s), 145.35 (d), 139.03 (d), 135.01 (d), 132.88 (d), 81.23 (s), 56.11 (d), 53.99 (d), 52.94 (d), 48.50 (d), 48.13 (t), 44.44 (t), 43.61, 42.89 (d), 15.93 (q).

***exo*-3-*n*-Hexylbicyclo[2.2.1]hept-5-en-2-one (IVb-x). Procedure B.** Alkylation of II-D with *n*-hexyl iodide was complete in 15 min to give hexyl hydrazone VIb (>10:1 single isomer presumably *E*) in 87% yield after vacuum distillation (bp 105–110 °C (0.5–1 mm)). ^{1}H NMR: δ 6.30 (dd, *J* = 6, 3, 1 H), 6.05 (dd, *J* = 6, 3, 1 H), 3.12 (m, 1 H), 2.87 (m, 1 H), 2.38 (s, 6 H), 2.20 (m, 1 H), 1.95–1.50 (bd, AB pattern, J_{AB} = 9 Hz, 2 H), 1.30 (m, 10 H), 0.90 (t, 3 H, Me). ^{13}C NMR: δ 176.44 (s, C-2), 139.97 (d, C-5), 134.55 (d, C-6), 50.28 (d, C-1), 46.99 (q, NMe_2), 45.52 (t, C-7), 44.80 (d, C-3/C-4), 44.22 (d, C-3/C-4), 31.84, 29.71, 29.26, 28.69, 22.67 (all t), 14.11 (q, Me). Acid hydrolysis (30 min) gave hexyl ketone IVb-x after vacuum distillation (bp 80–85 °C (0.5 mm)) in 78% yield from VIb. IVb: IR 1750 (s), 1460 (m), 1320 (m), 1133 (m), 760 (m), 733 (m), cm^{-1}; ^{1}H NMR δ 6.56 (dd, *J* = 5.6, 2.5 Hz, 1 H, H-5), 6.15 (m, 1 H, H-6), 2.96 (m, 2 H, H-1, H-4), 2.10 (m, 2 H, H-7s and H-7a), 1.84–1.62 (m, 2 H), 1.42–1.21 (m, 9 H), 0.88 (bt, 3 H, Me); ^{13}C NMR δ 216.9 (s, C-2), 143.9 (d, C-5), 131.86 (d, C-6), 55.66 (d, C-1), 47.28 (t, C-7), 45.71 (d, C-3), 43.81 (d, C-4), 31.69, 30.88, 29.21, 28.32, 22.63 (t, CH_2), 14.07 (q, Me).

Procedure A. Trimer Vb. Alkylation of enolate II (0.01 mol) with hexyl iodide was allowed to proceed for 3 h at room temperature to give one major spot on TLC (R_f 0.49; 4:1, P/E). FCC (10:1, P/E) gave trimer Vb (0.11 g, 8% yield) from 1.5 g of crude reaction product. Shorter reaction times are expected to give higher trimer yields. The stereochemical details of Vb have not been established. A second reaction was allowed to proceed for 18 h with TLC monitoring and at least eight components detected. FCC (20:1, P/E) gave IVb-x (0.049 g,[7] 2.5% yield). A second FCC (1:1, P/E) on the residue gave the dimer of I and II (0.61 g, 5% yield) of unestablished stereochemistry. Trimer Vb: ^{1}H NMR δ 6.70 (dd, *J* = 6, 3 Hz, 1 H), 6.25 (m, 2 H), 6.00 (dd *J* = 6, 3 Hz,

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1 H), 5.75 (m, 1 H), 5.70 (s, 1 H, OH), 4.30 (s, 1 H, OH), 3.0–1.8 (m), 1.60–1.10 (m), 0.90 (bt, 3 H, Me); ^{13}C NMR δ 222.12 (s, C-2), 145.12, 142.00, 139.78, 133.86, 133.73, 133.28 (d, C-5, C-5′, C-5″, C-6, C-6′, C-6″), 84.57, 81.85 (s, C-2′, C-2″), 55.60, 55.27, 52.74, 52.18, 48.68, 46.83, 45.18, 43.20 (all d, C-1, C-1′, C-1″, C-3, C-3′, C-3″, C-4, C-4′, C-4″) (one resonance in the 55–43 ppm region was not observed due to overlap) 49.21, 48.84, 45.85 (t, C-7, C-7′, C-7″), 32.07, 30.23, 29.79, 29.71, 22.75 (t, CH_2), 14.13 (q, Me). Dimer of I and II: ^{1}H NMR δ 6.70 (dd, J = 6, 3 Hz, 1 H), 6.43 (dd, J = 6, 3 Hz, 1 H), 6.20 (dd, J = 6, 3 Hz, 1 H), 6.08 (dd, J = 6, 3 Hz, 1 H), 3.50 (m, 1 H), 3.20 (m, 2 H), 2.85 (m, 1 H), 2.55 (m, 1 H), 2.20–0.90 (m, 8 H); ^{13}C NMR 213.45, 141.81, 138.96, 133.85, 127.34, 80.81, 57.47, 55.69, 50.97, 50.46, 48.71, 43.61, 42.67, 41.74.

Alkylation of II with Allyl Bromide. Preparation of Trimer Vc. Procedure A. Alkylation of II (0.01 mol) in THF (30 mL) with allyl bromide (1.5 equiv) was run at −78 °C and warmed to room temperature. Within a few minutes at room temperature, TLC showed complete consumption of ketone I. Workup and FCC (10:1, P/E) gave the trimer Vc (0.58 g, 48% yield; mp 120–123 °C, recrystallized from EtOH). This single compound was characterized by high-resolution 200-MHz NMR (32K data points, 1400-Hz SW, 2.3-s AT with resolution enhancement). Homonuclear COSY (256 × 1024 data matrix, 90°-t-60°-acq sequence, Gaussian weighting both dimensions) established the coupling connectivities which were further verified in a NOESY sequence (256 × 1024 data matrix; (90°-t_2-90°-0.15-90°-acq-10-)$_4$ pulse sequence).

Heteronuclear COSY conditions were 6640 Hz × 1400 Hz as a 2048 × 512 data matrix; J = 150 Hz using the HETCOR pulse sequence.[30] Gaussian weighting was employed in both dimensions. Proton T_1 measurements were made on 0.2–1 M solutions in $CDCl_3$ at 23 °C. A 1500-Hz spectral window, 6K data points, and (-180°-t-90°-acq-10-)$_{16}$ pulse sequence were used. The resolved peaks in each multiplet were frequency selected, and T_1 was evaluated by using the instrumental semilogarithmic fitting routine.[30] The intensities with 0.01-s delay were equal and opposite in sign to the intensities with 15-s delay to within ±10% with the zero delay intensity consistently smaller. The instrumentally determined errors were ±2% on signals free of overlap and usually agreed even more closely for peaks within a multiplet. In overlapped regions the fit was ±10%. Experiments were run with different concentrations, and the T_1 was increased by a factor of 4 with increasing dilution consistent with decreasing solution viscosity. The T_1 data reported is for the lowest concentration (~0.2 M). The concentration-dependent T_1 increase at each position was the same within ±6%, confirming the intramolecular dipole–dipole relaxation mechanism. MS (EI, 70 eV): m/e (intensity) 298 (23.0, M − C_5H_6), 233 (18), 232 (89), 215 (19), 191 (13), 173 (24), 167 (18), 166 (73), 151 (10), 149 (15), 145 (20), 135 (31), 111 (22), 107 (60), 91 (41), 83 (19), 82 (34), 81 (19), 80 (16), 79 (78), 77 (55), 69 (49), 67 (42), 66 (100), 65 (18), 55 (35), 41 (30). MS (CI): m/e (intensity) 365 (2.2, M + H), 347 (36.4, M + H − H_2O), 282 (17), 281 (100, M + H − H_2 − C_5H_6), 215 (20), 201 (38), 135 (15). Anal. Calcd for $C_{24}H_{28}O_3$: C, 79.09; H, 7.74. Found: C, 79.01; H, 7.69.

Preparation of *exo*- and *endo*-3-Allylbicyclo[2.2.1]hept-5-en-2-one (IVc-x and IVc-n). Procedure A. The above reaction was repeated except that the mixture was heated to reflux after being warmed to room temperature. TLC showed that Vc had disappeared after 1 h. No further change occurred before workup after 4 h. FCC (20:1, P/E) gave IVc-x (30%) and IVc-n (10%). The ^{13}C chemical shifts at C-6 and C-7 gave the stereochemistry assuming a γ-gauche upfield shift. IVc-x: ^{1}H NMR δ 6.60 (dd, J = 6, 3 Hz, 1 H, H-5), 6.15 (dd, J = 6, 3 Hz, 1 H, H-6), 5.95–5.50 (m, 1 H, H2′), 5.10 and 4.90 (m, 2 H, H1′), 2.90 (m, 2 H, H-1 and H-4), 2.6–1.60 (m, 5-H); ^{13}C NMR δ 216.28 (s, C=O), 143.79 (d, C-5), 136.19 (d, C2′), 131.92 (d, C-6), 116.29 (t, C1′), 55.61 (d, C-1), 46.99 (t, C-7), 45.12 (d, C-3 or C-4), 43.11 (d, C-3 or C-4), 34.98 (t, C3′). IVc-n: ^{1}H NMR δ 6.50 (dd, J = 6, 3 Hz, 1 H, H-5), 6.10 (dd, J = 6, 3 Hz, 1 H, or H-6), 5.90–5.60 (m, 1 H, H-2′), 5.10 and 4.95 (m, 2 H, H1′), 3.00 (m, 2 H, H-1 and H-4), 2.70–1.60 (m, 5 H); ^{13}C NMR δ 215.13 (s, C=O), 140.61 (d, C-5), 136.33 (d, C2′), 130.25 (d, C-6), 115.77 (t, C-1′), 56.55 (d, C-1), 49.57 (t, C-7), 47.61 (d, C-3 or C-4), 42.81 (d, C-3 or C-4), 36.44 (t, C3′). Procedure B alkylation was not attempted with allyl bromide.

Enolate Alkylation and Benzyl Trimer Vd. Procedure A. Alkylation of enolate II with benzyl chloride at −78 °C and standing for 3 h at room temperature gave trimer Vd (13% yield) as the only identifiable product after FCC (4:1, P/E). Lower R_f materials were also present. ^{1}H NMR: δ 7.20 (m, 5 H), 6.70 (dd, J = 6, 3 Hz, 1 H), 6.45–6.00 (m, 5 H), 5.80 (m, 1 H), 5.85 (s, 1 H, OH), 4.50 (s, 1 H, OH), 3.20–2.20 (m, 13 H), 1.80–1.50 (m, 4 H). ^{13}C NMR: δ 222.19, 145.10, 141.95, 139.72, 134.03, 133.79, 133.28, 142.91, 129.09, 128.24, 125.60, 84.62, 81.83, 55.63, 55.57, 52.66, 52.09, 50.10, 49.25, 48.99, 45.49, 44.81, 44.48, 43.13, 36.61. One resonance in the 55–43 ppm region was not observed due to overlap.

Preparation of *exo*-3-Benzylbicyclo[2.2.1]hept-5-en-2-one (IVd-x). Procedure B. Alkylation of II-D with benzyl chloride took 30 min at −50 °C to give alkylated hydrazone VId in 85% yield after vacuum distillation (bp 110–115 °C (0.5–1 mm)) as a single isomer—presumably *E*. ^{1}H NMR: δ 7.3 (m, 5 H), 6.20 (m, 2 H), 3.90 (d, J = 13 Hz, 1 H), 3.20 (m, 1 H), 2.65 (m, 1 H), 2.45 (s, 6 H), 2.35–2.00 (m, 2 H), 1.90 (bd, J = 10 Hz, 1 H), 1.6 (bd, J = 10 Hz, 1 H). Mass spectrum (EI, 70 eV): m/e (intensity) 240 (M^+, 28), 196 (8), 159 (31), 130 (16), 125 (17), 91 (47), 72 (12), 65 (13), 45 (100), 44 (27). Acid hydrolysis gave benzyl ketone IVd-x in 83% yield after a 30-min reaction and vacuum distillation (bp 105–110 °C (0.5–1 mm)). The endo proton splitting by H-7s established stereochemistry. IR: 1745 (s), 1398 (m), 1353 (m), 1220 (m), 1130 (m), 987 (m), 935 (m), 809 (m), 750 (m), 733 (s), 698 (s), 668 (m) cm^1. ^{1}H NMR: δ 7.34–7.15 (m, 5 H), 6.47 (dd, J = 5.4, 2.0 Hz, 1 H), 6.14 (m, 1 H), 3.13 (dd, J = 13.8, 3.8 Hz, 1 H), 3.03 (m, 1 H), 2.87 (m, 1 H), 2.47 (dd, J = 13.9, 11.4 Hz, 1 H), 2.20–2.09 (m, 3 H). ^{13}C NMR: δ 216.73 (s), 143.87 (d), 139.87 (s), 131.91 (d), 128.71 (d), 128.53 (d), 126.31 (d), 55.81 (d), 47.44 (d), 46.87 (t), 42.80 (d), 36.69 (t).

Alkylation of Lithium *anti*-7-(Dimethoxymethyl)bicyclo[2.2.1]hepta-2,5-diene 2-Oxide (a-II). Procedure A. The enolate a-II was prepared and alkylated on a 0.092-mol scale in 150 mL of THF substituting keto acetal a-I[1,3] for I in procedure A. The reaction with methyl iodide took 2 h and gave a 3:1 mixture of *endo*- and *exo*-3-methyl-*anti*-7-(dimethoxymethyl)-bicyclo[2.2.1]hept-5-en-2-one (a-IVa-n and a-IVa-x) in 83% yield after vacuum distillation (70 °C (1 mm)). The isomers were separated by FCC (3:1, hexane:ethylacetate). The aldol dimer of a-Ia and a-II was isolated from the pot residue.

***anti*-7-(Dimethoxymethyl)-*endo*-3-methylbicyclo[2.2.1]-hept-5-en-2-one (a-IVa-n).** ^{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), 4.31 (d, J = 8 Hz, 1 H, $CH(OMe)_2$), 3.35 (s, 6 H, OMe), 3.00 (m, 2 H, H-1, H-4), 2.70 (bd d, J = 8 Hz, 1 H, H-7), 2.22 (qd, J = 7, {4}$_{3.0}$, 1 H, H-3 exo), 1.05 (d, J = 7, 3 H, Me). ^{13}C NMR: δ 215.42 (s, C-2), 142.2 (d, C-5), 130.63 (d, C-6), 102.07 (d, $CH(OMe)_2$), 63.07 (d, C-7), 57.53 (d, C-1), 54.31 (q, OMe), 52.34 (q, OMe), 45.99 (d, C-4), 38.60 (d, C-3), 16.51 (q, Me).

***anti*-7-(Dimethoxymethyl)-*exo*-3-methylbicyclo[2.2.1]-hept-5-en-2-one (a-IVa-x).** ^{1}H NMR: δ 6.70 (dd, J = 6, 3 Hz, 1 H, H-5), 6.20 (dd, J = 6, 3 Hz, 1 H, H-6), 4.36 (d, J = {9}$_{2.7}$, 1 H, $CH(OMe)_2$), 3.35 (s, 6 H, OMe), 3.00 (m, 2 H, H-1, H-4), 2.70 (bd d, J = 9 Hz, 1 H, H-7), 2.07 (dq, J = 8 Hz, {3}$_{2.7}$, 1 H, H-3 endo), 1.15 (d, J = 8 Hz, 1 H, Me). ^{13}C NMR: δ 218.87 (s, C-2), 145.45 (d, C-5), 132.09 (d, C-6), 101.50 (d, $CH(OMe)_2$), 63.92 (d, C-7), 57.25 (d, C-1), 54.33 (q, OMe), 51.58 (q, OMe), 46.91 (d, C-4), 38.81 (d, C-3), 14.43 (q, Me).

Aldol Dimer (a-Ia + a-II). ^{1}H NMR: δ 6.75 (dd, J = 6, 3 Hz, 1 H), 6.40 (dd, J = 6, 3 Hz, 1 H), 6.23 (dd, J = 6, 3 Hz, 1 H), 6.00 (dd, J = 6, 3 Hz, 1 H), 5.15 (d, J = 9 Hz, 1 H), 4.25 (d, J = 8 Hz, 1 H), 3.35 (overlapping s, 12 H), 3.05 (m, 1 H), 2.90 (m, 1 H), 2.65 (m, 2 H)), 2.20 (m, 2 H), 1.60 (m, 2 H), 1.15 (d, J = 7 Hz, 3 H, Me). ^{13}C NMR: δ 211.42, 143.85, 142.79, 135.54, 126.52, 102.35, 102.06, 80.09, 63.58, 57.96, 54.64, 54.25, 52.74, 52.34, 49.20, 49.20, 44.25, 43.19, 14.70. (The two additional resonances are presumably overlapped in the 57–43 ppm region.)

***endo*-3-Hexyl-*anti*-7-(dimethoxymethyl)bicyclo[2.2.1]-hept-5-en-2-one (a-IVb-n).** The hexyl adduct was prepared on a 0.05-mol scale using *n*-hexyl iodide as alkylating agent and the above procedure with 50 h reaction time. Volatiles were removed by distillation to give crude product (10.4 g). FCC (2:1, P/E) of

(30) Varian XL-200 Generation H software.

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, CH(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, CH(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, CH(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, CH((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).

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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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