microcrystalline **22**: 0.46 g; mp 183–230 °C; $[\alpha]^{25}_{589}$ −15.95°, $[\alpha]^{25}_{578}$ −17.66°, $[\alpha]^{25}_{546}$ −23.33°, $[\alpha]^{25}_{435}$ −90.81° (*c* 1.11, THF). Anal. Calcd for $C_{22}H_{16}O_3$: C, 80.48; H, 4.91. Found: C, 80.54; H, 5.09). A second crystallization of these crystals from benzene gave microcrystalline **22**: 0.14 g; mp 250–257 °C; $[\alpha]^{25}_{589}$ −4.02°, $[\alpha]^{25}_{578}$ −4.57°, $[\alpha]^{25}_{546}$ −5.91°, $[\alpha]^{25}_{435}$ −22.44° (*c* 1.27, THF). A final crystallization of the product obtained from benzene gave microcrystalline **22**: 80 mg; mp 252–258 °C; $[\alpha]^{25}_{589}$ −2.02°, $[\alpha]^{25}_{578}$ −2.09°, $[\alpha]^{25}_{546}$ −2.71°, $[\alpha]^{25}_{435}$ −10.54° (*c* 1.29, THF). Concentration to 7 mL of the benzene filtrate obtained from the first crystallization described above gave light yellow crystals of **22** upon standing: 0.40 g; mp 190–192 °C; $[\alpha]^{25}_{589}$ −24.41°, $[\alpha]^{25}_{578}$ −26.31°, $[\alpha]^{25}_{546}$ −34.95°, $[\alpha]^{25}_{435}$ −136.31° (*c* 1.11, THF). Anal. Calcd for $C_{22}H_{16}O_3$: C, 80.48; H, 4.91. Found: C, 80.58; H, 5.02. Recrystallization of this material from benzene gave **22**: 0.30 g; mp 191–193 °C; $[)\alpha]^{25}_{589}$ −23.98°, $[\alpha]^{25}_{578}$ −26.10°, $[\alpha]^{25}_{546}$ −34.39°, $[\alpha]^{25}_{435}$ −134.63° (*c* 1.23, THF). A third crystallization of this product from benzene gave **22**: 0.20 g; mp 191–193 °C; $[\alpha]^{25}_{589}$ −23.71°, $[\alpha]^{25}_{578}$ −25.93°, $[\alpha]^{25}_{546}$ −34.07°, $[\alpha]^{25}_{435}$ −133.43° (*c* 1.08, THF).

The combined crystals and filtrates of **22** (.70 g) from the optically enriched samples described above were dissolved in 25 mL of refluxing absolute ethanol. To this hot solution was added a hot solution of 0.70 q of quinidine in 25 mL of absolute ethanol. The resulting solution was concentrated to 20 mL. Three recrystallizations from absolute ethanol of the crystals that separated gave a salt of constant melting point and specific rotation: mp 200–206 °C; $[\alpha]^{25}_{589}$ +63.21°, $[\alpha]^{25}_{578}$ +64.90°, $[\alpha]^{25}_{546}$ +71.94°, $[\alpha]^{25}_{435}$ +91.03° (*c* 1.23, THF). Decomposition of this salt was accomplished by washing a solution of it in 30 mL of 1:1 Et_2O/benzene with five portions of aqueous 10% HCl and one portion of aqueous $NaHCO_3$. The organic layer was dried ($MgSO_4$) and concentrated to give a foam which crystallized when dissolved in 5 mL of benzene. The white crystals obtained were dried (56 °C (0.5 mm) 36 h) to give (−)-(*S*)-**22**: mp 190–193 °C; $[\alpha]^{25}_{589}$ −25.98°, $[\alpha]^{25}_{578}$ −28.28°, $[\alpha]^{25}_{546}$ −37.21°, $[\alpha]^{25}_{435}$ −145.3° (*c* 1.22, THF). Anal. Calcd for $C_{22}H_{16}O_3$: C, 80.48; H, 4.91. Found: C, 80.71; H, 5.31.

Chair–Twist Equilibria in Some *tert*-Butyl Octalones

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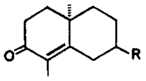
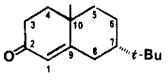
The solution conformations of four bicyclic enones, 7α-*tert*-butyl-10β-methyl-$\Delta^{1,9}$-octalone (**3**), its 7β-epimer (**4**), and the isomeric 6β- (**5**) and 6α-*tert*-butyloctalones (**6**), have been examined with ^{13}C and high-field ^1H NMR in conjunction with molecular mechanics calculations. Enones **4** and **6** were chosen as references in which ring B exists as a normal chair with an equatorial substituent. Enone **5** was used as a model in which ring B exists in a twist conformation with a ψ-equatorial *tert*-butyl group. Enone **3** is conformationally heterogeneous, with a significant contribution from the chair conformer bearing an axial *tert*-butyl group.

During an investigation of the conformation of epi-α-cyperone (**1**), we prepared enone **2**, a *tert*-butyl analogue of this well-known intermediate for sesquiterpene synthesis. Although it was assumed that enone **2** would exist predominently if not exclusively, with the ring bearing the *tert*-butyl group in a twist conformation, experimental data concerning the conformation were contradictory. Neither CD nor lanthanide shift ^1H NMR data for **2**, when compared to those of **1** and various derivatives of **1**, were particularly informative. The ^{13}C NMR spectrum of **2** seemed to indicate that the preferred conformation was that with an axial *tert*-butyl appended to a chair (or deformed chair) cyclohexane ring while the crystal structure of the oxime of enone **2** indicated a twist conformation with a ψ-equatorial *tert*-butyl group. High-field ^1H NMR spectra were best interpreted in terms of an equilibrium mixture containing greater than 50% of a nonchair conformer.[1] The study of the conformation of enone **2** was complicated somewhat by the lack of availability of the stereoisomer bearing an equatorial *tert*-butyl group and suitable model compounds in which ring B could be safely assumed to be in a twist conformation.



1 R = CH_2=CCH$_3$
2 R = *t*-Bu
10 R = *i*-Pr



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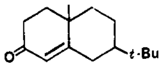

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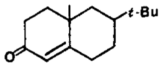

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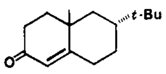

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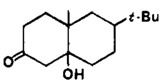

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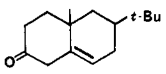

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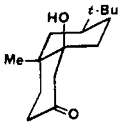
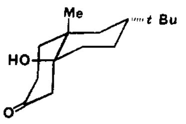


7a



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For many years it was considered that a cyclohexane ring would invariably adopt a twist conformation in preference to a chair bearing an axial *tert*-butyl substituent;[2] however, recent work has provided a number of examples in which conformationally mobile cyclohexane derivatives exist either partially or completely in a chair conformation with an axial *tert*-butyl group.[3] Enone **2** and related compounds appeared to be suitable substrates for an investigation into steric effects governing the chair–twist equilibrium in bicyclic systems bearing a potential axial

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(1) Huffman, J. W.; Swain, W. E.; Jacobus, J.; McPhail, A. T. *J. Org. Chem.* **1980**, *45*, 3088.

(2) Eliel, E. L. "Stereochemistry of Carbon Compounds"; McGraw-Hill: New York, **1962**; Chapter 8.

(3) (a) Goldsmith, D. J.; Thottathil, J. K. *J. Org. Chem.* **1982**, *47*, 1382. (b) Vierhapper, F. W.; Eliel, E. L. *Ibid.* **1979**, *44*, 1081. (c) Hargrave, K. D.; Eliel, E. L. *Tetrahedron Lett.* **1979**, 1987. (d) Van der Graff, B.; von Bekkum, H.; van Been, A.; Wepster, B. M.; von Wijke, A. M. *Recl. Trav. Chim. Pay-Bas* **1974**, *93*, 137. (e) Van der Grall, B.; Baas, J. M. A.; Wepster, B. M. *Ibid.* **1978**, 97, 268. (f) Geneste, P.; Kamenka, J. M.; Roques, R.; DeClerey, J. P.; Germain, G. *Tetrahedron Lett.* **1981**, *22*, 949.

0022-3263/84/1949-4943$01.50/0

Table I. ^{13}C **Chemical Shifts of Enones 3–6**[a]

C	compd			
	3	4	5	6
1	126.14	124.43	124.67	123.82
2	199.32	199.50	199.62	199.44
3	34.18	34.06	34.37	33.94
4	36.20	37.90	39.61	38.45
5	37.60	41.68	34.67	42.84
6	21.45	22.79	40.71	43.08
7	45.03	49.42	25.84	28.21
8	31.99	34.25	29.19	33.09
9	174.03	171.29	174.70	170.56
10	36.01	35.59	36.62	36.13
CH_3	24.68	22.10	24.88	22.67
$C(CH_3)_3$	34.18	32.60	32.05	32.11
$C(CH_3)_3$	27.54	27.36	27.06	27.42

[a] All chemical shifts were determined at 25 °C with 0.91 M $CDCl_3$ solutions and are reported in ppm relative to Me_4Si (δ).

tert-butyl group as well as providing an assessment of the methods available for such studies.

Although enone **2** is a readily available compound[1], in order to simplify the synthesis of reference compounds in this series, the present study was carried out by using normethyl analogues of **2**, enones **3–6**.[4,5] This is justified as we had found previously that the ^{13}C spectra of enones **2** and **3** are identical, with the exception of obvious and predictable differences caused by the methyl at C-1.[1] Enone **4** is the analogue of enone **3** in which the preferred conformer is that in which the *tert*-butyl group is equatorial to a normal chair ring. Enone **5** is assumed to exist exclusively with ring B in a twist conformation[6] and enone **6** serves as a reference compound in which ring B exists in a chair conformation bearing an equatorial *tert*-butyl group.

The synthesis of enone **3** has been reported by House,[7] while its isomer, enone **4**, is available from the reaction of 1-pyrrolidino-4-*tert*-butyl-6-methylcyclohexene with MVK.[5] Although the spectral properties of **5** and **6** were discussed by Loomes and Robinson,[6] details of their preparation have not been published.[8] The normal stereochemical consequences of the Robinson annulation,[9] indicated that enone **5** should be readily available via reaction of 2-methyl-4-*tert*-butylcyclohexanone with MVK but that enone **6** would probably prove to be less readily accessible.

Reaction of 2-methyl-4-*tert*-butylcyclohexanone[10] with MVK afforded the expected ketol (**7**) plus a small amount of a pure enone, which on the basis of its ^{13}C NMR spectrum was **6**.[12] Dehydration of **7** afforded enone **5**, contaminated with a small amount of a nonconjugated isomer (**8**). The fortuitous isolation of enone **6** from the annulation is explicable in terms of the conformations of the precursors to enones **5** and **6**. The precursor of **5** (**7**) is locked in a conformation in which the β-hydroxyl group is equatorial to ring A while that of enone **6** is locked in a conformation in which the hydroxyl group is axial to ring A and anti to the 1α-hydrogen.

Previously, we found the most informative data concerning the conformation of enones **1** and **2** in solution to be ^{13}C and high-field ^1H NMR. Although difficulty was found in reconciling the data for enone **2**, both techniques appeared to provide a sensitive probe of the solution conformations of relatively complex molecules. The ^{13}C NMR signals for enones **3–6** (Table I) were assigned by standard techniques of off-resonance decoupling and selective deuteration.[1] The chemical shift data for enone **3** were consistent with those reported previously[1] and those for the ring carbons (C-1 through C-10) of enone **6** were in agreement with those calculated by Loomes and Robinson.[6,13] The data for enone **5** were in agreement with those reported with the exception of C-6, which we find at δ 40.8 rather than δ 44.8.[6]

A number of criteria for detecting significant contributions of twist conformers with ^{13}C NMR were noted by Loomes and Robinson[6] and had been previously employed in our investigation of enones **1–3** and **10**. Interpretation of the ^{13}C spectra of enones **5** and **6** by using these principles confirms that these enones have ring B in twist and chair conformations, respectively. In particular, the ring B carbons of enone **5** are, on the average, shielded by 2.0 ppm relative to those of enone **6**.[14] The *tert*-butyl methyls of **5** are slightly shielded relative to those of **6** and the angular methyl in enone **5** is deshielded relative to that of enone **6**.[6,15]

Application of similar criteria to enones **3** and **4** shows that the average chemical shifts of the B ring carbons of enone **3** are shielded by 1.5 ppm relative to those of enone **4** and the angular methyl of enone **3** is deshielded relative to that of enone **4**, indicative of a twist conformation for ring B. However, the *tert*-butyl methyl carbons of enone **3** are slightly deshielded relative to those of enone **4**, indicating some contribution from a ring B chair conformer with an axial *tert*-butyl group.[6]

An argument we had invoked previously as being indicative of a chair conformation for ring B in enone **2** was the fact that C-9 was *deshielded* relative to the same carbon in model compounds in which ring B was in a chair conformation. This deshielding was attributed to a syn-δ effect by one of the methyls of an axial *tert*-butyl group. However, C-9 in both enones **3** and **5** is deshielded relative

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(4) The nomenclature and numbering used are based on an octalone ring system, as depicted in **3**. The system of nomenclature employed in ref 1 was based on the eudesmane ring system and is not applicable to enones **5** and **6**.

(5) In particular the anomalous enamine alkylation sequence used to prepare enone **4** as described by Huffman, Rowe, and Matthews [Huffman, J. W.; Rowe, C. D.; Matthews, F. J. *J. Org. Chem.* **1982**, *47*, 1438] does not proceed cleanly with ethyl vinyl ketone.

(6) Loomes, D. J.; Robinson, M. J. T. *Tetrahedron* **1977**, *33*, 1149.

(7) House, H. O.; Lusch, M. J. *J. Org. Chem.* **1977**, *42*, 183.

(8) In ref 6, enone **6** is described as being available from the reaction of the "appropriate 9-hydroxy-2-decalone (available in this laboratory) with oxalic acid". Enone **6** was obtained only as a minor component of a mixture of unspecified composition. The reference cited for the preparation of this ketol and the mixture containing enone **6** is: Elliot, D. R. Ph.D. Thesis Liverpool, 1965. Presumably the ketol which serves as the precursor to enone **5** is 9β-hydroxy-6β-*tert*-butyl-10β-methyl-2-decalone (**7**), obtained by a Robinson annulation sequence similar to that described here.

(9) Jung, M. E. *Tetrahedron* **1976**, *32*, 3 has reviewed the Robinson annulation.

(10) Allinger, N. L.; Blatter, H. M. *J. Am. Chem. Soc.* **1961**, *83*, 994. In the initial alkylation of *o*-cresol with *tert*-butyl chloride, some difficulty was encountered in separating 2-methyl-4-*tert*-butylphenol from the 2,6-isomer, and oxidation of the mixture of stereoisomeric 2-methyl-4-*tert*-butylcyclohexanols could not be effected by using Jones reagent. The preparation of 4-*tert*-butyl-2-methylcyclohexanone is included as supplementary material in the microfilm edition.

(11) Marshall, J. A.; Fanta, W. I. *J. Org. Chem.* **1964**, *29*, 2501.

(12) The observed ^{13}C chemical shifts are in good agreement with the estimated values given in ref 6.

(13) In ref 6 no ^{13}C data are reported for the angular methyl or the *tert*-butyl carbons.

(14) In ref 6, a difference of 2.3 ppm is found, however the lack of availability of a pure sample of enone **6** precluded the application of any other criteria.

(15) The angular methyl group in enone **6** is axial with respect to both rings, and will have two γ-gauche interactions, with C-3 and C-6, while the angular methyl of enone **5**, in which ring B is predominantly in a twist conformation, will have only one γ-gauche interaction, that with C-3. This leads to the predictable and observed deshielding of the angular methyl in enone **5**, relative to that of enone **4**. For a discussion of the ^{13}C chemical shifts of methyl groups attached to cyclohexyl systems see: Dalling, D. K.; Grant, D. M. *J. Am. Chem. Soc.* **1967**, *89*, 6612.

to the same carbon in enones **4** and **6**. Since enone **5** should exist with ring B exclusively in a twist conformation, this deshielding must be caused by some factor other than that previously ascribed to it. The origin of this effect is not clear, but it may well be due to small conformational deformations of ring A in enones **3** and **5**.

It has been suggested that a particularly sensitive probe of possible chair–twist equilibria is the variation with temperature of ^{13}C chemical shifts of a compound which is locked in a chair conformation (e.g., **4** and **6**) and an epimer in which a chair–twist equilibrium is possible.[6] This approach is based on the observation that the twist conformer is favored entropically and that for a system in which such an equilibrium exists, an increase in temperature will increase the relative amount of twist conformer.[16] In practice, the ^{13}C chemical shifts of a pair of epimers are measured at two different temperatures, and the $\Delta\delta$ values at each temperature are compared and interpreted relative to the chemical shift differences expected for a change in the chair–twist equilibrium.[6]

The ^{13}C NMR spectra of enones **3–6** were determined at +50 and −50 °C, and are summarized in Table II (included as supplementary data in the microfilm edition). Surprisingly, the average changes in chemical shift for the ring B carbons of both pairs of enones (**3**, **4** and **5**, **6**) were nearly identical and less than half those found for the two isomers of 3,5-di-*tert*-butylcyclohexane.[6] It had been anticipated that there would be a considerably larger variation in chemical shifts for enone **3** in which an equilibrium was presumed to exist between chair and twist conformers than for enone **5** which should exist almost exclusively in a twist conformation. The only indication of the existence of this equilibrium for enone **3** is a slight increase in shielding of the *tert*-butyl methyl signals at 50 °C, consistent with a possible increase in the population of a twist conformer.

There are two a priori explanations for the lack of differences in rrelative chemical shifts with temperature for enones **3** and **5**. Either both enones are conformationally homogeneous at both temperatures or the twist conformation of ring B in enone **3** is considerably more constrained due to the fusion with ring A than the di-*tert*-butylcyclohexane studies by Robinson. This would decrease the entropy factors favoring a twist conformation relative to the chair and suppress considerably the effect of temperature on the chair–twist equilibrium.

To further explore the possible existence of such an equilibrium the 360-MHz ^1H NMR spectra of enones **3–5** and their 3,3-dideuterio derivatives (Table III) were determined.[17] The appropriate chemical shifts and coupling constants for enone **4** agreed well with those reported for enones **1** and **10** with normal chair conformations of ring B.[1] The coupling constants for the ring A protons ($J_{3,4}$) in enones **3** and **5** are somewhat different from those of enones **4** and **6** suggesting a slightly different conformation of ring A as a function of the conformation of ring B.[18]

Table III. ^1H **NMR Chemical Shifts and Coupling Constants for Enones 3–5**[a]

H	compd 3	compd 4	compd 5
$H_{3\beta}$	2.55	2.76	2.58
$H_{3\alpha}$	2.36	2.54	2.39
$J_{3\mathrm{gem}}$	17.9	16.8	17.8
$J_{3\beta4\alpha}$	14.0	10.8	13.9
$J_{3\beta4\beta}$	5.1	9.2	5.4
$J_{3\alpha4\beta}$	5.0	3.8	4.8
$J_{3\alpha,4\alpha}$	1.6	3.8	*b*
$H_{8\beta}$	2.44[c]	2.36	2.39
$H_{8\alpha}$	2.24[c]	2.53	2.20
$J_{8\mathrm{gem}}$	16.0	13.7	13.0
$J_{7\alpha,8\beta}$		13.5	9.9
$J_{7\beta,8\beta}$	7.0[d]		9.9
$J_{7\alpha,8\alpha}$		3.5	8.4
$J_{7\beta,8\alpha}$	3.1[d]		1.7

[a] All chemical shifts were determined at 360 MHz as $CDCl_3$ solutions and are reported in ppm relative to Me_4Si (δ). All coupling constants are in Hz. [b] br s. [c,d] Values are interchangeable.

Previously, we interpreted the high-field NMR spectra of enone **2** in terms of an equilibrium mixture containing 50–75% of a twist conformer.[1] This analysis was based on coupling constants for the ring B conformers of enone **2**, calculated by using the Karplus equation with dihedral angles obtained from Dreiding models. For the twist conformer the $H_{7,8}$ dihedral angles were estimated from the crystal structure of the oxime of **2**, and for the chair conformer it was assumed that ring B would have the same undistorted chair conformation as enones **1** and **10**. To refine this approach, the geometries of enones **2–6** were calculated with Allinger's MM 2 empirical force field program.[19,20] The calculated geometries of enones **4** and **6** indicate an undistorted chair conformation for ring B, with the dihedral angles involving the hydrogens at C-7 and C-8 within 3° of the normal angles for a chair cyclohexane.

The calculated structure for the ψ-equatorial conformer of enone **3** shows some slight variations from that of enone **2**, attributed to the presence of the methyl group at C-4 in the latter compound, and both are consistent with the crystallographic data for the oxime of **2**.[20] In contrast to our earlier assumption regarding the conformer of **2** with an axial *tert*-butyl group, the structure calculated by MM 2 shows considerable distortion (flattening) of ring B which results in the changes in the H_7–H_8 dihedral angles noted below. The ORTEP[21] structure is included as supplementary material in the microfilm edition. For enone **5**, Loomes and Robinson suggested a twist conformation for ring B in which the *tert*-butyl group was ψ-equatorial.[6] The calculated strain energy for this conformer is 3.4 kcal/mol less than that of the conformer with an isoclinal *tert*-butyl

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(16) (a) Allinger, N. L.; Freiberg, L. A. *J. Am. Chem. Soc.* **1960**, *82*, 2393. (b) Allinger, N. L.; Blatter, H. M.; Frieberg, L. A.; Karkowski, F. M. *Ibid.* **1966**, *88*, 2999.

(17) The 360-MHz spectrum of enone **6** showed a pattern of at least 18 lines between δ 2.28 and 2.42 due to the protons at C-8 and the equatorial proton at C-3. The axial proton at C-3 showed coupling constants almost identical with those of the same proton in enone **4**.

(18) The differences in coupling constants are not great enough to draw any firm conclusions regarding the ring A conformations, but these differences are probably responsible for the differences in CD curves between enones **1** and **2**,[1] but are not sufficient to cause any significant changes in the UV spectra of enones **3–6**, all of which show λ_{max} 240 ± 2 nm. These small conformational differences may be responsible for the unexplained deshielding of C-9 in enones **3** and **5** mentioned above.

(19) (a) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127. (b) *Quantum Chem. Prog. Exchan.* 395.

(20) Although MM 2 is not parameterized to produce reliable heat of formation data for conjugated systems, it will produce accurate structures and resonable strain energies for them. The calculated valence angles for the twist conformer of enone **2** are all within ±2° of those found experimentally for the oxime of **2** as described in ref 1. The average deviation of the calculated and crystallographic dihedral angles is ±1.7° and with the exception of the C4–C5–C6–C7 angle all are within ±3° of those found for the oxime **2** by crystallography. The calculated value for the C4–C7 dihedral angle is 155°, while that reported in ref 1 is 160°. This difference may arise from the use of MM 2 for a conjugated system but may equally well arise from structural differences caused by crystal packing in the solid state or by small structural differences between the oxime of **2** and **2** itself. The MM 2 program does not contain parameters to enable the calculation of structures containing C–N double bonds.

(21) Johnson, C. K. ORTEP Report ORNL-3794, revised. Oak Ridge National Laboratory, TN, 1965.

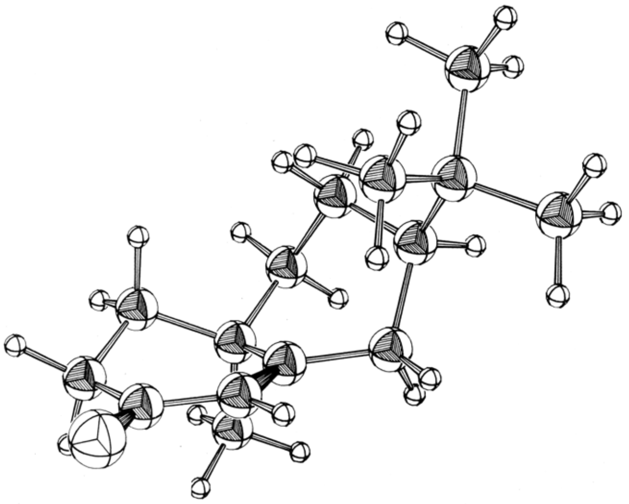

Figure 3. ORTEP drawing of enone **3**. Conformation with a twist ring B and isoclinal *tert*-butyl group.

group. The ORTEP structure, of enone **5**, derived from MM 2 is depicted in Figure 2, included as a supplementary material in the microfilm edition.

For enone **4**, with ring B in an unstrained chair conformation, $J_{7\alpha,8\alpha} = 3.5$ Hz and $J_{7\alpha,8\beta} = 13.5$ Hz, in general accord with the dihedral angles calculated by MM 2 (62° and 180°, respectively). Application of the Karplus relationship[22] gives calculated coupling constants of 2.2 and 16 Hz, however, it is known that coupling constants are affected by the electronegativity of substituents attached to the system being studied. These effects may be modified by altering the value of $J°$ in the Karplus equation,[23] and by using the experimentally determined coupling constants for enone **4**, combined with those found earlier for **10**, a $J°$ value of 13 is used for dihedral angles of 0–90°. For angles of 90–180°, a $J°$ value of 13.5 is used, based on the 180° dihedral angle between $H_{7\alpha}$ and $H_{8\beta}$ in enone **4**.[24]

When the dihedral angles generated by MM 2 for $H_{7\beta,8\beta}$ and $H_{7\beta,8\alpha}$ (35° and 81°, respectively) in enone **5** were used, calculated coupling constants of 8.7 and 0.3 Hz, respectively, are obtained. For $H_{7\alpha,8\alpha}$ and $H_{7\alpha,8\beta}$ the dihedral angles are 34° and 150° with calculated coupling constants of 8.4 and 9.9 Hz. These calculated values are all within 1.5 Hz of the experimentally determined values (Table III).

The dihedral angles calculated for $H_{7\beta,8\alpha}$ and $H_{7\beta,8\beta}$ for the ring B chair conformer of enone **3** (Figure 1) are 68° and 46°, with calculated coupling constants of 1.8 and 6.2 Hz, respectively. For the twist boat conformer bearing a ψ equatorial *tert*-butyl substituent the dihedral angles are 177° and 65°, with calculated coupling constants of 13.1 and 2.3 Hz. The observed coupling constants for these pairs of protons (Table III) are 7.0 and 3.1 Hz. Separate calculations using both sets of data indicate a conformational equilibrium containing either 46% or 79% of the twist conformer.

Although the large deviation in the equilibrium concentrations calculated from the two sets of data is perhaps not unreasonable given the inherent uncertainties in the use of the Karplus relationship, the molecular mechanics calculations provided an alternative explanation. While carrying out these calculations, we examined other twist conformers of enone **3**, in particular that bearing an isoclinical *tert*-butyl substituent (Figure 3) the calculated strain energy of which is 0.1 kcal/mol less than that of the twist conformer bearing a ψ-equatorial substituent. Using these data, one calculates a conformer population at 25 °C consisting of 40% of the chair conformer, 46% of that bearing an isoclinical *tert*-butyl group and 14% with the substituent ψ equatorial. The calculated dihedral angles and coupling constants for the conformer with an isoclinal *tert*-butyl group are 92° (0 Hz) and 24° (10.8 Hz) for $H_{7\beta,8\alpha}$ and $H_{7\beta,8\beta}$, respectively. The weighted average of the calculated coupling constants for the three contributing conformers gives $J_{7\beta,8\alpha} = 2.6$ Hz and $J_{7\beta,8\beta} = 7.8$, in good agreement with the observed values of 3.1 and 7.0 Hz.

This interpretation, which predicts 60% of the two twist conformers at equilibrium, is consistent with the ^{13}C data but is not consistent with the crystal structure for the solid-state conformation of the oxime of enone **2**.[1] However, the two twist conformers are interconverted by pseudorotation, and it is possible that crystal packing forces favor the conformer with the ψ-equatorial *tert*-butyl substituent, although it may be less stable in solution.

Of the various methods used to probe the solution conformations of these enones, the most sensitive appears to be a combination of high-field ^1H NMR combined with molecular mechanics calculations. Although the ^{13}C data are consistent with those obtained by these other methods, it is very difficult to clearly define the conformations of either enone **3** or **5** with ^{13}C in the absence of other experimental observations.

It should be noted that this constitutes a caveat regarding the extension of Loomes and Robinson's techniques[6] to systems significantly more complex than those in their original paper without confirmatory data obtained by other methods.

Experimental Section

Infrared spectra were obtained as neat films between salt plates, as solutions in carbon tetrachloride or chloroform, or as potassium bromide pellets with Perkin-Elmer Model 137 or 1310 infrared spectrophotometers. Routine ^1H NMR spectra were obtained on a Hitachi Perkin-Elmer Model R-24 (60 MHz) or JEOL FX-90Q (90 MHz) spectrometers with deuteriochloroform as solvent. High-resolution ^1H NMR spectra were obtained at Emory University with a Nicolet 360 NB (360-MHz) spectrometer with deuteriochloroform as solvent. ^{13}C NMR spectra were obtained on a JEOL FX-90Q spectrometer operating at 22.5 MHz with deuteriochloroform as solvent. Both ^{13}C and ^1H NMR spectral data are reported in parts per million (δ) relative to Me_4Si. Ultraviolet spectra were obtained in 95% ethanol solution on Perkin-Elmer Model 202, Cary-14, or Bausch & Lomb 2000 spectrophotometers. GLC analyses were performed on an F & M Model 810 instrument or Perkin-Elmer Sigma 3B Dual FID Chromatograph with a Sigma 15 Chromatography Data Station utilizing a flame-ionization detector. Columns used included a 2 ft × 0.125 in. OV-101 and a 6 ft × 0.125 in. 10% SE-30 on 80–100 mesh Chromosorb W and a 9 ft × 0.125 in. OV-17 on 80–100 mesh Chromosorb W. Mass spectral analyses were performed on a Hewlett-Packard 5985 Gas Chromatograph/mass spectrometer at 70 eV with a 2 ft × 0.125 in. 2% OV-101 column on 100–200 mesh Chromosorb WHP. Melting points, which are not corrected, were obtained using a Kofler hot stage apparatus. Elemental analysis were performed by Atlantic Microlab, Inc., Atlanta, GA.

7β-*tert*-Butyl-10β-methyl-$\Delta^{1,9}$-2-octalone (3). This enone was prepared by the reaction of the pyrrolidine enamine of 5-

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[22] Bhacca, N. S.; Williams, D. H. "Applications of NMR Spectroscopy in Organic Chemistry"; Holden-Day: San Francisco, **1964**; pp 49–51. See also: Williamson, K. L.; Johnson, W. S. *J. Am. Chem. Soc.* **1961**, *83*, 4623.

[23] Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,", 2nd ed; Pergamon: Oxford, **1969**, pp 281–284 and many references therein.

[24] The average *e, e* and *e, a* coupling constants in enones **4** and **10** is 3.5 Hz, which would give a *J* value of 14. However, it is generally accepted that $J°$ for angles less than 90° is less than that for those between 90° and 180° (Abraham, R. J.; Holker, J. S. E. *J. Chem. Soc.* **1963**, 806).

[25] The ORTEP structure is essentially identical, save for obvious differences, to the structure of the oxime of enone 2 reported in ref 1.

tert-butyl-2-methylcyclohexanone and methyl vinyl ketone as described previously.[5] The ^{13}C and ^{1}H NMR data are summarized in Tables I and III, respectively.

6α-*tert*-Butyl-10β-methyl-$\Delta^{1,9}$-2-octalone (6) and 6β-*tert*-Butyl-9β-hydroxy-10β-methyl-2-decalone (7). To 5.00 g (29.7 mol) of 4-*tert*-butyl-2-methylcyclohexanone at 0 °C was added 1 mL of 3.5 M ethanolic sodium ethoxide followed by the dropwise addition of 2.52 g (36 mol) of freshly distilled methyl vinyl ketone. A second 1 mL of 3.5 M sodium ethoxide was then added, followed by the dropwise addition of an additional 0.5 g of methyl vinyl ketone and the reaction mixture was allowed to stand at −13 °C for 72 h. After warming to ambient temperature, the reaction mixture was partitioned between ether and saturated aqueous NH_4Cl. The aqueous phase was extracted with ether, and the combined etheral extracts were washed with brine and dried and the solvent was removed to give 6.73 g of a viscous oil. Flash chromatography[26] on silica gel with ether–hexanes as eluent gave 0.246 (4%) of 6α-*tert*-butyl-10β-methyl-$\Delta^{1,9}$-2-octalone (**6**) as a colorless oil which was homogeneous to GLC, but which slowly decomposed on standing: IR 1668, 1620 cm^{-1}; UV λ_{max} 238 (log ϵ 4.10); mass spectrum *m/e* (relative intensity) 220 (100), 205 (13), 192 (28), 178 (30, 164 (53), 163 (50); ^{1}H NMR δ 0.80 (s, 9 H, $C(CH_3)_3$), 1.15 (s, 3 H, CH_3), 5.64 (s, =CH). The ^{13}C NMR data and the balance of the ^{1}H data are summarized in Tables I and II, respectively.

The semicarbazone formed white crystals from methanol, mp 204–206 °C. Anal. Calcd for $C_{16}H_{26}N_3O$: C, 69.28; H, 9.81; N, 15.15. Found: C, 69.07; H, 9.83; N, 15.07.

The more polar material from the original reaction mixture was dissolved in ethyl acetate–benzene (5:95) and chromatographed on silica gel. Elution with ethyl acetate–benzene (3:7) gave, after recrystallization from hexanes, 0.794 g (11%) of ketol **7**. The analytical sample: mp 139–141 °C crystallized from hexanes; IR 3496, 1701 cm^{-1}; H NMR δ 0.86 (s, 9 H, $C(CH_3)_3$, 1.20 (s, 3 H, CH_3); mass spectrum *m/e* (relative intensity) 238 (5), 220 (2), 168 (100), 126 (24), 125 (24), 112 (19). Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99. Found: C, 75.62; H, 11.02.

6β-*tert*-Butyl-10β-methyl-$\Delta^{1,9}$-2-octalone (5). To a solution of 0.067 g of NaOH in 7 mL of water and 14 mL of methanol was added 0.400 g of ketol **7** in 27 mL of methanol and the mixture was heated at reflux under N_2 for 23 h. The cooled reaction mixture was diluted with brine, concentrated in vacuo, and extracted with ether. The ethereal extracts were washed with brine and dried and the solvent was removed at reduced pressure to give 0.420 g of a yellow oil. Distillation (140 °C (air bath), 2.4 mm) followed by chromatography on silica gel and elution with ether–hexanes gave 0.300 g (81%) of octalone **5** contaminated with 15% of the β,γ-isomer **8**. For octalone **5**: IR 1651 cm^{-1}; UV λ_{max} 240 nm (log ϵ 4.02); ^{1}H NMR 0.79 (s, 9 H, $C(CH_3)_3$), 1.18 (s, 3 H, CH_3), 5.76 (s, 1 H, =CH). The balance of the ^{1}H NMR and ^{13}C NMR data are summarized in Tables III and I, respectively. Mass spectrum, *m/e* (relative intensity) 220 (66), 205 (7), 192 (28), 178 (19), 164 (38), 163 (54), 149 (37), 136 (53), 123 (54), 122 (58), 121 (100).

The 2,4-dinitrophenylhydrazone formed orange crystals from ethanol–ethyl acetate, mp 160–162 °C. Anal. Calcd for $C_{21}H_{18}N_4O_4$: C, 62.98; H, 7.05; N, 13.99. Found: C, 62.73; H, 7.24; N, 12.68.

Nonconjugated enone **8**: IR 1710 cm^{-1}; ^{1}H NMR 80.84 (s, 9 H, $C(CH_3)_3$), 130 (s, 3 H, CH_3); mass spectrum, *m/e* (relative intensity) 220 (100), 205 (14), 192 (20), 165 (31), 164 (62), 163 (50), 149 (48), 147 (18), 146 (18), 145 (33).

Deuterium Labeling Procedures. Labeling under basic conditions was carried out using NaOD in D_2O/dioxane as described previously.[1] Labeling under acidic conditions was carried out using DCl or D_2SO_4 in diglyme also using previously described procedures.[1]

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Supplementary Material Available: Table II, ^{13}C chemical shifts of enones **3**–**6** at +50 and −50 °C, ORTEP structures of the ring B chair conformer of enone **3** and enone **5** (Figures 1 and 2), and the experimental details for the preparation of 4-*tert*-butyl-2-methylcyclohexanone (4 pages). Ordering information is given on any current masthead page.

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Synthesis of Smectic Liquid-Crystalline Polysiloxanes from Biphenylcarboxylate Esters and Their Use as Stationary Phases for High-Resolution Gas Chromatography

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Eight new liquid-crystalline compounds based on the 4-(4-hydroxyphenyl)benzoate ester have been prepared. These compounds all exhibit liquid-crystalline characteristics. The new compounds all contain an olefinic group needed for attachment to a siloxane polymer. The polysiloxanes prepared by a hydrosilylation reaction also exhibited liquid–crystalline characteristics. A copolymer prepared from equal molar amounts of two of the liquid–crystalline alkenes was found to have unique separating properties when used as a stationary phase in high–resolution gas chromatography.

A large number of polymers containing mesogenic side chains and a polysiloxane backbone have been prepared and characterized.[1–6] The use of a flexible spacer to decouple the motions of the mesogenic groups from the polymer main chain has allowed the preparation of thermotropic liquid crystals exhibiting both smectic and ne-

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