

are of much lower quality and resolution.<sup>12-20</sup> From high resolution proton and deuterium magnetic resonance studies of the  $\text{ND}_4^+$ ,  $\text{ND}_3\text{H}^+$ , and  $\text{NH}_4^+$  ions in acidified middle phases of the decylsulfate detergent, we were able to demonstrate the distortion of the ammonium ion from  $T_d$  symmetry in the oriented edl.<sup>4</sup> In this present study we report results for  $\text{BF}_4^-$  and  $\text{NH}_4^+$  simultaneously oriented in the edl of a cationic detergent system and resolve four quartets for the fluorine nuclei in  $\text{BF}_4^-$ . A middle phase of the following composition is typical of those studied, 45.5 wt %  $\text{D}_2\text{O}$  (0.1 M HCl), 49.2% decylammonium tetrafluoroborate, and 5.3% ammonium tetrafluoroborate. The previous study<sup>4</sup> of ammonium ions in an anionic detergent employs opposite charges for the mobile and relatively immobile detergent ions. In the present work the cationic detergent middle phase is shown to cause ordering of both small tetrahedral cations ( $\text{NH}_4^+$ ) and anions ( $\text{BF}_4^-$ ).

In Figure 1 the fluorine and boron magnetic resonance spectra of the  $\text{BF}_4^-$  ion in the middle phase described above is presented for a probe temperature of 29.7°. All the spectral parameters measured from  $^{11}\text{B}$ ,  $^{19}\text{F}$ ,  $^1\text{H}$ , and  $^2\text{H}$  nmr spectra are listed in the legend to the figure. Of special note are the following. (a) The  $\Delta\nu_{\text{QD}}$  of the  $\text{ND}_4^+$  cation in a cationic phase is larger than previously measured in the anionic middle phase<sup>4</sup> and this indicates, surprisingly, a higher degree of distortion. (b) There is a separation in the  $^{19}\text{F}$  spectrum of +18.0 Hz at 41° between isotropic and nematic phases. (c) When the isotropic micellar and middle nematic phases coexist between 41 and 44°, the value  $|(J + D)_{\text{BF}}|$  remains constant at  $3.16 \pm 0.05$  Hz but this value increases linearly to  $7.05 \pm 0.05$  Hz as the temperature is lowered to 17.5° through the nematic range. (d) The  $|J_{\text{BF}}|$  is  $0.61 \pm 0.05$  Hz in normal isotropic or micellar solution.

There is now considerable evidence from spectra of the oriented  $\text{ND}_3\text{H}^+$  ion in the present work that the assignment of the magnitude of  $D_{\text{NH}}$  in this ion was incorrectly reported in the previous study.<sup>4</sup> Comparing the dependence of  $|(J + D)_{\text{NH}}|$  on phase composition with relative variations in  $\Delta\nu_{\text{QD}}(\text{ND}_4^+)$ ,  $\Delta\nu_{\text{QD}}(\text{D}_2\text{O})$ ,  $\Delta\nu_{\text{QH}}(\text{BF}_4^-)$ , and  $\Delta\nu_{\text{QD}}(-\text{ND}_3^+)$ ,<sup>21</sup> it is clear that  $D_{\text{NH}}$  is of opposite sign to the absolutely positive  $J_{\text{NH}}$  and takes the small values rather than values around -100 Hz. Taking  $(D + J)_{\text{NH}} = 50.55 \pm 0.05$  Hz from the figure legend and  $J_{\text{NH}} = +52.23$  Hz,  $D_{\text{NH}}$  becomes -1.68 Hz. A full report on distortion of tetrahedral ions will be published soon.

**Acknowledgment.** Research supported by operating funds provided by the National Research Council of

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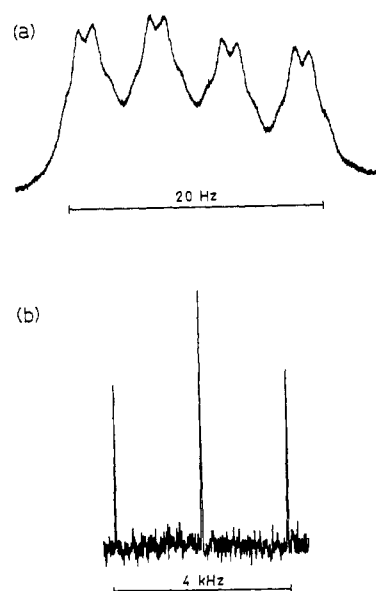
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**Figure 1.** (a)  $^{19}\text{F}$  nmr spectrum of the  $\text{BF}_4^-$  ion in the cationic detergent middle phase mentioned in the text. The main observable 1:1:1:1 quadruplet with separation  $|(J + D)_{\text{BF}}|$  is the sum of the scalar and dipole-dipole coupling between  $^{11}\text{B}$  and  $^{19}\text{F}$  in the ion. The further splitting into 1:3:3:1 quadruplets arises because of an average distortion of the tetrahedron. The separations give  $D_{\text{FF}}$ , the dipole-dipole coupling between fluorine atoms in the ion. Intensities are distorted in the low field side of the spectrum because of underlying isotopically shifted  $^{10}\text{BF}_4^-$  signals. (b) The  $^{11}\text{B}$  spectrum of the same sample at the same temperature demonstrates a typical 3:4:3 first-order quadrupole splitting, which arises because of anisotropic tumbling and distortion of the local  $T_d$  symmetry at the  $^{11}\text{B}$  nucleus. Spectral parameters are:  $|(J + D)_{\text{BF}}| = 5.75 \pm 0.02$  Hz,  $\delta_{\text{F}} = 1554.3$  (downfield from external  $\text{C}_6\text{F}_6$  capillary),  $|D_{\text{FF}}| = 0.71 \pm 0.05$  Hz,  $2 \Delta\nu_{\text{QB11}} = 3.77 \pm 0.01$  kHz (separation of outer components of  $^{11}\text{B}$  3:4:3 triplet),  $\Delta\nu_{\text{QD}}(-\text{ND}_3^-) = 7.14 \pm 0.05$  kHz (quadrupole splitting for terminal ionic head deuterium nuclei in the edl of the cationic detergent),  $|(D + J)_{\text{NH}}| = 50.55 \pm 0.05$  Hz (scalar plus dipole-dipole coupling of the  $\text{ND}_3\text{H}^+$  ion from proton spectrum),  $\Delta\nu_{1/2} = 12$  Hz (half width of components of  $\text{ND}_3\text{H}^+$  proton spectrum),  $\Delta\nu_{\text{QD}}(\text{ND}_4^+) = 87 \pm 1$  Hz (quadrupole splitting for deuterium in  $\text{ND}_4^+$  ions), and  $\Delta\nu_{\text{QD}}(\text{D}_2\text{O}) = 239 \pm 1$  Hz (quadrupole coupling for deuterium in the water).

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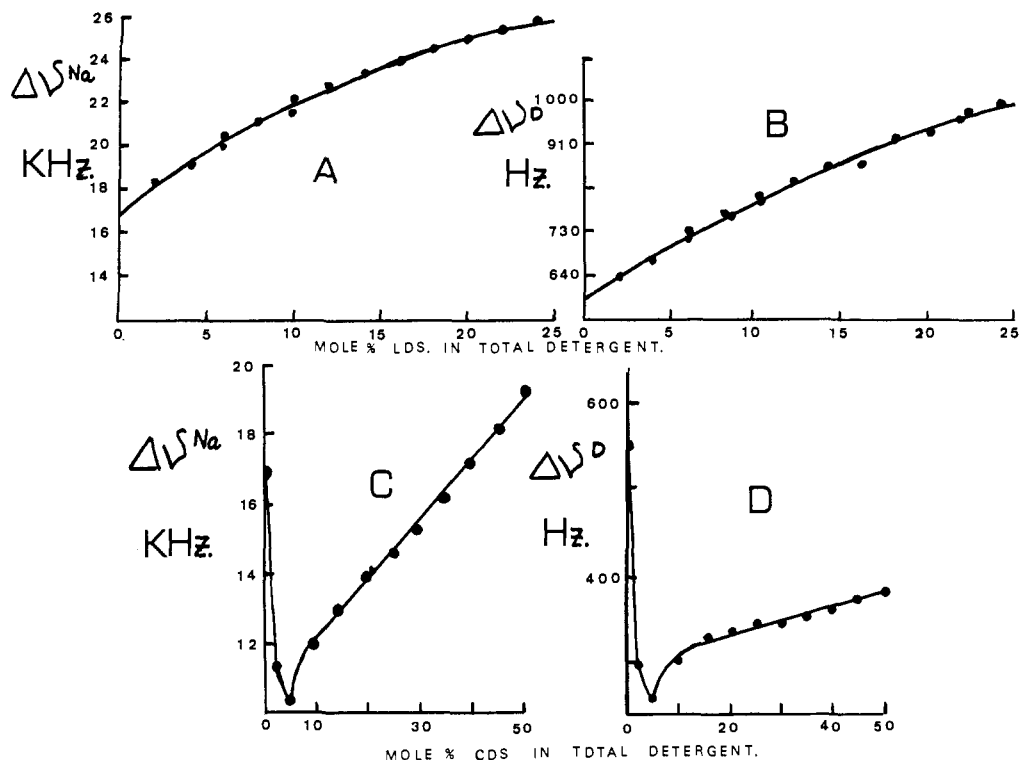
## Studies of Membrane Processes. VI. Monatomic Ions in the Electrical Double Layer

Sir:

It is now well known from work on alkali metal and deuterium magnetic resonance<sup>1-9</sup> studies in biological

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**Figure 1.** (A) Sodium-23 nuclear quadrupole splittings between the outer peaks of the 3:4:3 triplet of the nuclear magnetic resonance spectrum " $\Delta\nu^{Na}$ " as the mole per cent of LDS in the LDS-SDS mixture is increased. Middle phases have constant molar composition: detergent-decanol-water. Phases become increasingly viscous with increasing LDS content and require longer and longer periods to orient in the magnetic field. (B) Deuterium quadrupole splittings for the same phases as in (A) but derived from the  $D_2O$  in the aqueous region " $\Delta\nu^D$ ." (C) Sodium-23 quadrupole splittings  $\Delta\nu^{Na}$  for phases prepared from cesium decyl sulfate (CDS) and SDS mixtures with constant molar compositions: detergent-decanol-water. Phases initially become less viscous and subsequently increase in viscosity as CDS proportion is increased. (D) Deuterium quadrupole splitting  $\Delta\nu^D$  for phases prepared in (C) of the  $D_2O$  in the aqueous region.

material and lamellar liquid crystalline systems that first- and second-order quadrupole splittings of the nuclear Zeeman levels are a valuable tool in probing the orientation and mobility of constituents of a membrane interface. In our own work<sup>3,10-18</sup> the model systems studied are derived from the middle phases, which form single-crystal liquid crystalline materials in the magnetic fields used in the nmr experiment. The homogeneously ordered electrical double layer (edl)

provides high resolution nmr spectra of any nucleus under study, removes the complications of the range of order of microcrystallites,<sup>7,9</sup> and allows study of the composition of the edl even with a spinning sample tube to average out field inhomogeneities. Viewing the model system thus, we report here systematic variations in composition of alkali metal ions in the aqueous region with simultaneous measurement of nuclear quadrupole splittings for several nuclei in the same homogeneously oriented edl.

Middle phases of constant molar composition of detergent, water, and decanol but with mixed alkali metal ion detergents have been prepared. The molar composition of the master phase 37 wt % sodium decyl sulfate (SDS), 7 wt % decanol, and 56%  $D_2O$  was preserved in all phases, but lithium decyl sulfate (LDS) or cesium decyl sulfate (CDS) was substituted for SDS on a mole for mole basis. In what follows mole per cent of LDS or mole per cent of CDS refers to the mole per cent of these detergents substituted for SDS and is expressed as if the mole per cent of total detergent is 100%. In the total phase the mole per cent of LDS or CDS expressed as a fraction of the total number of moles of water, decanol, and detergents is of course much smaller.

Sodium and deuterium magnetic resonance and spectra exhibit partially averaged quadrupole couplings  $\Delta\nu^{Na}$  and  $\Delta\nu^D$  and these have been measured for middle phases prepared from  $Li^+-Na^+$  and  $Na^+-Cs^+$  mixed detergents. In Figure 1  $\Delta\nu^{Na}$  and  $\Delta\nu^D$  are obtained for these phases as a function of detergent composition in

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the phase. Substitution of LDS for SDS in the mixture increases the viscosity of the middle phase and the figure shows that this is accompanied by large increases in  $\Delta\nu^{\text{Na}}$  and  $\Delta\nu^{\text{D}}$ . Of striking note is the parallelism in the behavior of these two parameters in both LDS-CDS and SDS-CDS phases. No obvious macroscopic observation indicates a phase change at the critical value of 5 mol % CDS substituted for SDS (Figure 1C and D). The structure of the edl changes continuously or discontinuously with changes in mobile ion composition and this is reflected in both  $\Delta\nu^{\text{Na}}$  and  $\Delta\nu^{\text{D}}$ . Simple ion competition arguments involving sites at the detergent ion interface are not sufficient to explain these results.<sup>3,9</sup> The range of order for the middle phases used here is essentially infinite.<sup>9</sup>

If there is preferential ordering of mobile ions or water this can be expressed as ratios of partially averaged quadrupole couplings, because we may assume that static nuclear quadrupole couplings in the rigid equivalent solid state are invariant.<sup>19</sup>

$$\frac{\Delta\nu^{\text{Na}}}{\Delta\nu^{\text{D}}} = \left( \frac{2\nu_Q^{\text{Na}}}{\nu_Q^{\text{D}}} \right) \frac{S_{\text{Na}}}{S_{\text{D}}} \quad (1)$$

$\gamma_Q^{\text{Na}}$  and  $\gamma_Q^{\text{D}}$  are from the notation of Cohen and Reif.<sup>19</sup>  $S_{\text{Na}}$  and  $S_{\text{D}}$  are degrees of orientation for the sodium ion and  $\text{D}_2\text{O}$  in the aqueous layer along appropriate axes. Any increase in the degree of orientation of the sodium ion over that of the water as the detergent composition changes causes an increase in  $(\Delta\nu^{\text{Na}}/\Delta\nu^{\text{D}})$ .

In CDS-SDS middle phases this ratio increases linearly from 29.5 to 38 as  $\text{Cs}^+$  substitution goes from 0 to 5% then it breaks discontinuously to increase between 38 and 49 as  $\text{Cs}^+$  increases to 50%. Thus we conclude that  $\text{Na}^+$  replaces  $\text{D}_2\text{O}$  in the more ordered regions of the detergent surface and this is accompanied by overall structural changes in the Stern and diffuse layers.<sup>20</sup>

Corresponding ratios  $(\Delta\nu^{\text{Na}}/\Delta\nu^{\text{D}})$  for the LDS-SDS system indicates an opposite effect with a linear decrease from 29.5 to 25.8 as  $\text{Li}^+$  replaces  $\text{Na}^+$  to the extent 25%. There is no discontinuous break in the edl structure in this case and slight preference for water at the detergent interface as the  $\text{Li}^+$  increases follows from the ratio measurements. Large increases in macroscopic viscosity lead to considerably increased orientation times for these phases in the magnetic field. The angular dependence of the quadrupole splittings becomes possible using fast Fourier transform observation methods. The experiments give an angular dependence according to<sup>19</sup>

$$\Delta\nu = A(3 \cos^2 \Omega - 1) \quad (2)$$

for both deuterium and lithium-7 signals.  $\Omega$  becomes zero angle along the magnetic field direction for both signals.  $A$  is a constant. It is interesting that the direction of maximum orientation of both nuclei in the ordered phase is identical and that this direction corresponds to that of the magnetic field axis. It is possible that all middle phases behave in a similar manner but that often lower viscosities allow rapid reorientation in the field so that sample spinning becomes possible. It is difficult to reconcile this result with the cylindrical

superstructure arrays which have been proposed for middle phases.<sup>21</sup>

In the table are presented single crystal type quadrupole splittings ( $\Omega = 0$ ) for  $^7\text{Li}$ ,  $^{23}\text{Na}$ , and  $^2\text{H}$  for different compositions of LDS-SDS. All quadrupole couplings increase indicating a structure creating mechanism as  $\text{Li}^+$  replaces  $\text{Na}^+$ . Changes in ratios of quadrupole couplings (Table I) are not large and for

Table I. Partially Averaged Quadrupole Splittings for Lithium, Deuterium, and Sodium<sup>a</sup>

% LDS	$\Delta\nu^{\text{Li}}$ , Hz	$\Delta\nu^{\text{D}}$ , Hz	$\Delta\nu^{\text{Na}}$ , kHz	$\Delta\nu^{\text{Na}}/$ $\Delta\nu^{\text{D}}$	$\Delta\nu^{\text{D}}/$ $\Delta\nu^{\text{Li}}$	$\Delta\nu^{\text{Na}}/$ $\Delta\nu^{\text{Li}}$
12	345 ± 8	821	22.6	27.5	2.4	65.5
16	369.5 ± 6	886	23.8	27.0	2.40	64.7
20	381.7 ± 2	942	24.9	26.4	2.47	65.3
24	394.3 ± 2	983	25.5	26.0	2.49	64.7

<sup>a</sup> Nmr signals from middle phases prepared with LDS-SDS mixed detergents in total mol %: 57%  $\text{D}_2\text{O}$ , 36% detergent, 7% decanol. The percent of LDS in the detergent mixture is listed in the first column. Temperature is 29.1 ± 0.5°.

the phases measured they are close to the experimental error. The dominant effect on the edl in this case appears not to be ion competition for the detergent counterion interface but structural changes, which are not directly linked with any competitive equilibrium model.<sup>9</sup>

Addition of electrolytes to edl situations has been extensively studied *via* the electrokinetic potential.<sup>22</sup> In middle phases, such additions as sodium sulfate, ammonium chloride, etc., lead to impressive decreases in the viscosity of mesophases and such effects in colloidal systems have been characterized as the "electroviscous effect."<sup>22,23</sup> In the present study an nmr study of the electroviscous effect was achieved by adding lithium sulfate as an electrolyte to a middle phase consisting of SDS- $\text{D}_2\text{O}$ -decanol up to 6% by weight  $\text{Li}_2\text{SO}_4$ . Both sodium and deuterium quadrupole splittings decrease strongly with additions of as little as 0.6%  $\text{Li}_2\text{SO}_4$ , but at this point a two-phase system separates. After 1.04%  $\text{Li}_2\text{SO}_4$  has been added, a single birefringent phase forms once again, and up to 6% added electrolyte the sodium quadrupole splitting increases from 11.14 to 12.64 kHz, the deuterium splitting from 237.6 to 609.4 Hz, and the lithium-7 splitting remains constant at 173 ± 3 Hz. The phases are all much more mobile than LDS-SDS systems without added electrolyte. The electroviscous effect in this case is evidently accompanied by insignificant changes in the lithium ions location but a strong preference for the water in the more ordered regions and small changes in the sodium ion order. The overall decrease in quadrupole couplings indicates a much looser structure in the edl. We have outlined here a multinuclear magnetic resonance approach to many problems involving colloids edl and membrane phenomena, which is free of the difficulties inherent in systems which have a limited range of order. Considerable further work is continuing and results with other ion combinations

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such as Na<sup>+</sup>-K<sup>+</sup> will be published in a full paper along with a fuller description of this study.

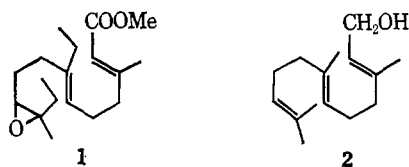
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### Stereoselective Epoxidations of Acyclic Allylic Alcohols by Transition Metal-Hydroperoxide Reagents. Synthesis of *dl*-C<sub>18</sub> Cecropia Juvenile Hormone from Farnesol

Sir:

We report here a stereoselective synthesis of *dl*-C<sub>18</sub> Cecropia juvenile hormone (1) from the readily available (*E,E*)-farnesol (2). A synthesis of 1 from farnesol



by a route involving nonstereoselective homologations has been reported previously.<sup>1</sup> Our approach depends crucially on the transition metal catalyzed epoxidation of olefinic alcohols by *tert*-butyl hydroperoxide.<sup>2</sup>

Having recently shown that transition metal catalyzed epoxidations of cyclic olefins by *tert*-butyl hydroperoxide are highly stereoselective,<sup>2a</sup> we have now found that these same reagents also effect stereoselective epoxidation of acyclic olefinic alcohols. Examination of the results in the table reveals that both the vanadium<sup>3</sup> and the molybdenum-*tert*-butyl hydroperoxide reagents are generally more selective in epoxidations of acyclic allylic alcohols than the previously reported peracid epoxidations<sup>4-6</sup> of these same substrates. The ratios of the diastereomeric epoxy alcohols reported in Table I using peracids were also determined in this study; these values correlate well with the reported literature values<sup>4,5</sup> using the same or

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(3) We would like to make an important correction to our previous publication<sup>2a</sup> on these oxidations. In the earlier work, epoxidation of 20 g of geraniol is carried out at reflux in benzene using the VO(acac)<sub>3</sub> catalyst. We have since found that most of the vanadium-catalyzed epoxidations of allylic alcohols proceed readily at room temperature, whereas the molybdenum systems do require heating. In contrast to the procedure described previously<sup>2a</sup> for the vanadium system, we recommend that the *tert*-butyl hydroperoxide (use 1.5 equiv instead of the 1.1 equiv recommended previously) be added slowly to the other reactants while stirring at room temperature; cooling is often necessary for large scale reactions. These milder conditions for the vanadium-catalyzed epoxidations should prove valuable when optimization of regio- and/or stereoselectivity is important (see also footnote g in table).

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**Table I.** Stereochemistry of Epoxidations of Acyclic Allylic Alcohols

Olefin <sup>a</sup>	Peracids <sup>b</sup>				<i>t</i> -BuOOH			
	NPBA		MCPBA		VO(acac) <sub>3</sub> <sup>d</sup>		Mo(CO) <sub>6</sub> <sup>e</sup>	
	T <sup>c</sup>	E	T	E	T	E	T	E
	64	36	64	36	71	29	53	47
	9	91			<1	>99	2	98
	32	68	20	80	2	98	2	98
			38	62	4 (<1) <sup>g</sup>	96 (>99) <sup>g</sup>		
			62	38	90	10	97	3
	96	4	96	4	82	18	96	4
			80	20	94	6	85	15

<sup>a</sup> The olefinic alcohols were obtained from Chemical Samples Co. The pure (*E*)-3-penten-2-ol was separated from its (*Z*)-isomer by distillation (bp 56° (70 mm)) through a Perkin-Elmer NFA-200 autoannular still. All epoxidations were performed on 5 mmol of the olefin dissolved in 25 ml of solvent. The product mixtures were analyzed by glc on a 50 ft Carbowax K20M SCOT capillary column. <sup>b</sup> The *p*-nitroperbenzoic acid (NPBA) epoxidations were performed at 0° in ether and the *m*-chloroperbenzoic acid (MCPBA) cases at 0° in methylene chloride. <sup>c</sup> T = % threo; E = erythro. <sup>d</sup> The VO(acac)<sub>3</sub> reactions were run at room temperature in benzene with ~5 mg of catalyst and 7.5 mmol (1.5 equiv) of *t*-BuOOH (94% Lucidol Division of Pennwalt Corp.). The *t*-BuOOH was dissolved in benzene and added slowly dropwise to the stirred reaction mixtures. <sup>e</sup> With the exception that the Mo(CO)<sub>6</sub> cases were run at reflux in benzene, the procedure was identical with that described for the VO(acac)<sub>3</sub> cases. <sup>f</sup> The threo and erythro epoxy alcohol diastereomers separated poorly (glc) in this case. Thus in order to confirm the assigned ratios and also the stereochemical assignments, the epoxy alcohol product mixtures were converted to mixtures of *threo*- and *erythro*-2,3-dihydroxyoctane by reaction with excess (8 equiv) lithium di-*n*-butylcuprate. The authentic 2,3-dihydroxyoctanes were prepared by osmylation of *cis*- and *trans*-2-octene, respectively. <sup>g</sup> The figures within the parentheses are the improved selectivities observed recently when the oxidation was carried out in toluene at 0° using 2 equiv of *t*-BuOOH. This result suggests that subambient temperatures ought to be explored whenever greater selectivity is desired in these epoxidations.

similar peracids on the same olefinic substrates. Of special interest for the synthesis of hormone 1 is the observation that epoxidation of the allylic alcohols 3 and 7 with the VO(acac)<sub>3</sub>-*t*-BuOOH reagent produces the erythro epoxy alcohols selectively. The erythro epoxy alcohol 4 on treatment with excess lithium dibutylcopper in ether at -26° for 2 hr was converted to vicinal diol 5 in 82% over-all yield.<sup>7</sup> Stereospecific deoxygenation of diol 5 was accomplished by the procedure of Eastwood and coworkers.<sup>8</sup> The diol was treated with *N,N*-dimethylformamide dimethyl acetal at 25° for 12 hr and the resulting dioxolane derivative

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