consequence of its cis-fused bicyclo[3.3.0]octane-like character.[5,17] Finally, while the stereoinductive effect of the C-2 methyl could not be confidently predicted, it could be correlated with the angle A assumed in the formation and/or further reaction of the exciplex. For angles between 0 and 30°, a clear preference for a β-methyl orientation would be expected on the basis of this model.

The arenealkene **5** required for the cedrene study and, in general, a wide range of aryl-substituted alkenes are readily prepared in an exceptionally straightforward and preparatively useful manner by using the procedure of Hall and co-workers.[18] Thus, *in one operation*, 2-chloro-5-methylanisole was converted to its lithio derivative which was treated with 6-methylhept-5-en-2-one; condensation of ammonia into the resulting mixture and addition of excess lithium provided the starting material for the photolysis, **5**, in 74% yield (distilled).[19] Irradiation of **5** in pentane (~0.13 M; milligram to multigram quantities) at room temperature using Vycor-filtered light from a 450-W Hanovia source proceeded with the gradual disappearance of **5** [NMR ($CDCl_3$) δ 3.80 (OCH_3)] and concomitant appearance of largely, if not exclusively, two cycloadducts [NMR ($CDCl_3$) δ 3.36 and 3.32 (OCH_3)]. After complete disappearance of starting material (ca. 12 h), these compounds (**3**:**4** = 1:1)[20] were isolated in a combined yield of 65%. Subsequent treatment of this mixture with 4 N HCl/acetone (1:4)[15c] provided cedren-11-one (**2**) along with its Δ^9 isomer. A more effective method for effecting the conversion of both cycloadducts to a single product (**2**) involved treatment of a mixture of **3** and **4** with bromine (1 equiv in CH_2Cl_2) which by electrophilic attack on the double bond induced cleavage of the cyclopropane ring and resulted in the formation of only 10α- and 10β-bromocedren-11-one. The absence of the corresponding tertiary allylic bromides in this reaction is an expected consequence of the facile rearrangement of such intermediates to the more stable secondary allylic bromide isomers. After removal of solvent in vacuo, the bromides were treated without isolation with neat tri-*n*-butyltin hydride (2 equiv) to give **2** in 59% overall yield.[21] Wolff–Kishner reduction of this product provided (±)-α-cedrene (**1**), free of any isomeric product, as established by its comparison with commercially available cedrene.[22] This structural assignment was further afforced by spectroscopic comparison of the crystalline alcohols obtained from the hydroboration of racemic and natural α-cedrene.[23]

The facility and effectiveness of this chemistry (cedrene in four steps), the increasing predictability of such arene–olefin cycloadditions, and the number and variety of potential applications of this methodology beyond this initial exercise in total synthesis clearly suggest a significant role for this cycloaddition in organic synthesis. Further studies are in progress.

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(17) The interactions between centers 5 and 1 and 6 and 7 in the exciplex or transition state may be considered as part of a five-membered ring. The resulting cis-fused bicyclo[3.3.0]octane-like subunit would be expected to be more stable than the trans isomer by analogy with the parent ring system (cf. Barret, J. W.; Linstead, R. P. *J. Chem. Soc.* **1936**, 611).

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(19) All new compounds reported were homogeneous by TLC and gave satisfactory IR and NMR spectra and exact mass and combustion analyses. Analytical data for selected intermediates are as follows. Photoadduct **3**: partial NMR ($CDCl_3$) δ 5.37 (m, 1 H), 3.31 (s, 3 H), 2.53 (br s, 1 H), 1.77 (d, J = 1.5 Hz, 3 H), 1.00 (s, 3 H), 0.89 (s, 3 H), 0.88 (d, J = 6.8 Hz, 3 H); mass spectrum (70 eV), *m/e* (% base peak) 232 (M^+, 18), 149 (B), 110 (21); high-resolution mass spectrum *m/e* 232.18274 (calcd 232.18271). Anal. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.61; H, 10.56. Photoadduct **4**: partial NMR ($CDCl_3$) δ 5.55 (br s, 2 H), 3.35 (s, 3 H), 1.32 (s, 3 H), 1.02 (d, J = 6.9 Hz, 3 H), 1.00 (s, 6 H); mass spectrum (70 eV) 232 (M^+, 16), 149 (B), 110 (19); high-resolution mass spectrum, *m/e* 232.18272 (calcd 232.18271). Anal. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.69; H, 10.49. Ketone **2**: partial NMR ($CDCl_3$) δ 5.36 (m, 1 H), 2.08 (s, 1 H), 1.73 (q, J = 1.9 Hz, 3 H), 1.16 (s, 3 H), 0.87 (s, 3 H), 0.85 (d, J = 7.1 Hz, 3 H); IR (film) 1735 cm^{-1}; mass spectrum (70 eV) *m/e* 218 (M^+, 84), 163 (69), 135 (B); high-resolution mass spectrum, *m/e* 218.16709 (calcd 218.16706). Anal. Calcd for $C_{15}H_{22}O$: C, 82.52; H, 10.16. Found: C, 82.46; H, 10.20.

(20) That these compounds are related as vinylcyclopropane isomers was demonstrated by the thermal (GC: T_{inj} = 250 °C; T_{col} = 190 °C or pyrolysis at 205–230 °C) conversion of **4** to **3** (cf.: Simpson, J. M.; Rickey, H. G. *Tetrahedron Lett.* **1973**, 2545 and ref 1).

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A Type I Aqueous Cholesteric Lyomesophase

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Cholesteric thermotropic liquid crystals[1] have a twist or helical axis, and using opposed optical enantiomers, they exist with the helices of opposite sign.[1-3] The relationship to nematic states is important, and it was shown that equimolar mixtures of opposite enantiomers of cholesteric mesophases became nematic.[1,4] Nematic phases align spontaneously in magnetic fields, and thermotropic nematics align almost exclusively with the director along the magnetic field direction.[5] This has been called type I behavior, i.e., $\Delta\chi > 0$ for the mesophase.[6] Very recently a new class of nematic thermotropic mesophases was discovered with type II properties[7] (with $\Delta\chi < 0$); they align with the director perpendicular to the magnetic field. It is clear that these magnetic susceptibility properties, besides providing a classification for nematic materials, imply that there are two corresponding types of cholesteric mesophases.[3] Balanced enantiomeric mixtures can yield type I or type II nematics, depending on the type of cholesteric phases from which they are derived.[8] While type II nematics of the thermotropic variety were only recently discovered,[7] as far as the authors are aware, there is only one report of true aqueous lyotropic type II cholesteric.[8] While Radley and Saupe[9] and Diehl and Tracey[10] added small amounts of optically active compounds to nematic lyotropic systems to induce a twist, these workers did not prepare a racemic amphiphile mixture to regenerate the balanced nematic system, and the majority of the amphiphiles in the micelle were not chiral compounds.

Some years ago it was shown that two cholesteric forms must exist,[3] the distinction being that the helical axis, although always

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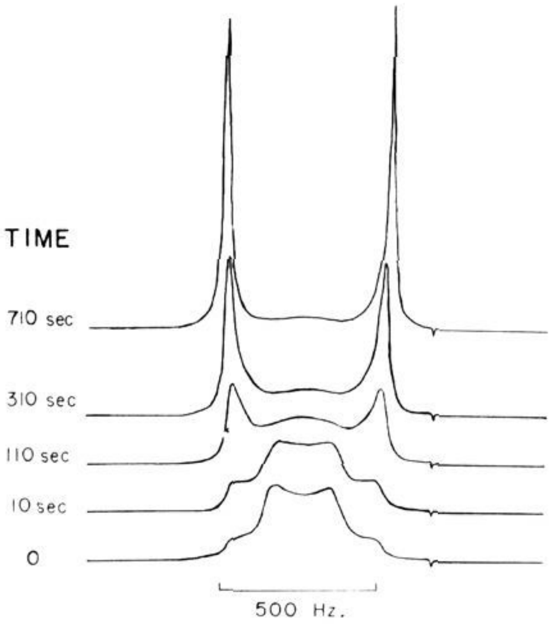

Figure 1. Deuterium NMR spectra of the D_2O component of the cholesteric type I lyomesophase as a function of time. The spectra relate to stages in the process of unwinding of the cholesteric twist by the action of the magnetic field. This unwinding is essentially complete after 710 s in the 58.75-kG field at 25 °C.

oriented perpendicular to the director of the related nematic form, is in the case of type II cholesterics aligned along the magnetic field with no untwisting effect by action of the field.[3] On the other hand, there is a tendency of type I cholesterics to be subject to an untwisting action of the magnetic field, since the helical axis tends to align perpendicular to the magnetic field. In the type I cholesteric thermotropic liquid crystals, the effect of the untwisting as a function of applied field has been studied[3,11] but the dynamics of the process has not.

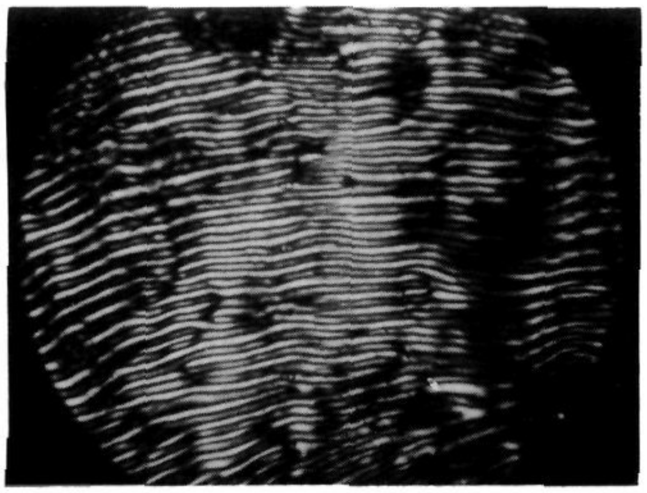

Figure 2. Cholesteric texture observed microscopically between crossed polaroids at 22.2 °C. Sample thickness was 0.2 mm, magnification 100×. The magnetic field was not applied to the sample.

Aqueous lyotropic systems of nematic liquid crystals are based on the orientational order of disk- or rodlike micelles.[12-14] These have been named type II DM (disk micelles) and type I CM (cylindrical micelles) on the basis of the sign of the magnetic susceptibility anisotropy. The absolute classification as nematic systems is still in doubt because some positional order of the micelles can be detected[14] which depends on the size and character of the containing vessel. We recently reported the first type II lyotropic cholesteric system based on use of pure resolved optically active amphiphiles and, furthermore, illustrated the important relationship of the balanced enantiomer mesophase to the type II nematic system.[8] The helix axis was shown to align along the field direction by studies of polarized microscopy and deuterium NMR of the included D_2O. The balanced optical isomers gave a type II DM mesophase.[8] It is the purpose of this report (a) to show the successful synthesis of a type I cholesteric lyotropic system, (b) demonstrate that the racemic mixture forms a type I CM liquid crystal, (c) provide a photomicrograph of the texture, and (d) show deuterium NMR spectra during the unwinding of the helix in the magnetic field, a dynamic process not hitherto accessible to study in the widely known thermotropic crystals. The composition of the mesophase is (wt %) potassium lauroyl-L-alaninate (D/L racemic mixture for the nematic system) 29.73, potassium sulfate 3.04, 1-decanol 4.8, and D_2O 62.43. The deuterium NMR spectra (for the D_2O signal) of the L mesophase are reproduced in Figure 1. A Bruker WM-250 spectrometer operating at 38.3 MHz equipped with a cryogenic magnet was used to register spectra at 25 °C. The deuterium signals were recorded at 1 ms and 10, 110, 310, and 710 s after placing the sample in the field; the spectra at increasing time are shown from the bottom upward (Figure 1). The racemic mixture of the synthetic detergent formed a type I CM nematic system, and this was verified by standard methods in a separate experiment.[6,15] The initial powder doublet[13] at 1 ms has very rounded features, indicating a high intrinsic line width of the constituent doublet components. The untwisting of the helix is almost complete after 710 s, and the constituent peaks of the doublet can be seen to have this rather large line width on the order of 16% of the powder pattern splitting in the lower spectrum. Further studies are in progress to quantify this new kinetic effect in terms of line shapes. The typical cholesteric texture was observed in the polarizing microscope (Figure 2), and further studies of the screw pitch are in progress. The detergent prepared for this study also shows type II cholesteric behavior in other regions of the phase diagram.

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Radical Coupling of Mercaptide Ligands upon Oxidation of Organometallic Mercaptide Complexes

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We have reported the characterization of 17e mercaptide complexes $[Fe(C_5H_5)(dppe)SPh]PF_6$ (dppe = 1,2-bis(diphenylphosphino)ethane)[1] and $[Fe(C_5H_5)(PMe_3)_2SPh]PF_6$.[2] These complexes were prepared by oxidation of an appropriate 18e precursor using mild oxidizing agents, the ease of oxidation reflecting the electron-rich character of these species. We have also prepared $[Fe(C_5H_5)[P(OPh)_3]_2SPh]BF_4$.[3] These complexes are blue and paramagnetic; they have magnetic moments of ~1.9 μ_B, appropriate for low-spin d^5 metal complexes.

The oxidation of $Fe(C_5H_5)(CO)_2SPh$ is in striking contrast to this work. When an acetone solution of this complex is treated with $NOPF_6$, NO evolves and an orange solid is obtained (69% yield). Analyses[4] of this material indicate the formula $[Fe(C_5H_5)(CO)_2SPh]PF_6$, but the compound is diamagnetic. An NMR spectrum (CD_3CN) shows a singlet resonance for cyclopentadienyl protons along with a multiplet in the phenyl proton region. Two ν(CO) absorptions (KBr disk) occur at 2060 s and 2025 s cm^{-1} which are appropriate for $[Fe(C_5H_5)(CO)_2L]^+$ complexes. The most reasonable formula which accords with these data is dimeric, having $Fe(C_5H_5)(CO)_2$ groups linked by a bridging diphenylsulfide ligand, viz.

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