Table I. Structural and Vibrational Parameters of Octahalodirhenate(III) Ions

complex	bond dist, Å	stretching freq,[d] cm^{-1}	emprcl force const,[e] mdyne/Å	diatomic force const,[f] mdyne/Å
$Re_2F_8^{2-}$ (M-M)	2.20[a]	318	4.56	5.55
$Re_2F_8^{2-}$ (M-X)	1.95[a]	623	3.68	4.35
$Re_2Cl_8^{2-}$ (M-M)	2.22[b]	274	4.32	4.12
$Re_2Cl_8^{2-}$ (M-X)	2.32[b]	361	2.95	2.73
$Re_2Br_8^{2-}$ (M-M)	2.23[c]	276	4.19	4.18
$Re_2Br_8^{2-}$ (M-X)	2.47[c]	211	1.93	2.10

[a] Present work. [b] Reference 3. [c] Reference 4. [d] Frequencies and assignments from ref 5. [e] Calculated from the following equations and appropriate interpolations:[14,15] first row (Li-Ne), $D = 1.04 + 0.607 \exp(-F/9.28)$; second row (Na-Ar), $D = 1.80 + 0.732 \exp(-F/2.66)$; third row (K-Kr), $D = 1.81 + 1.22 \exp(-F/2.37)$; fifth row (Cs-Rn), $D = 2.01 + 1.31 \exp(-F/2.36)$; Re-F, $D = 1.53 + 0.907 \exp(-F/4.778)$; Re-Cl, $D = 1.90 + 0.948 \exp(-F/3.60)$. ($D$ = bond distance, Å; F = force constant, mdyne/Å). [f] Calculated from the following equation (ν in cm^{-1}, μ in atomic mass units): $F = \nu^2\mu(5.9 \times 10^{-7})$, where $\mu = 93.1$ for the Re-Re stretch and μ = (halide mass) for the Re-X stretch.

van der Waals. From these relationships it is possible to estimate the Re-Re and Re-X force constants from the EXAFS or crystallographic bond distances. It is also possible to calculate these force constants from the symmetric Re-Re and Re-X stretching frequencies in the RR spectra. To the extent that these stretching vibrations are unmixed with one another and with the remaining symmetric coordinate of $Re_2X_8^{2-}$ (the Re-Re-X angle bend), it is appropriate to calculate the force constants from the stretching frequencies by using the diatomic approximation. Indeed, the precision of the empirical correlations, 0.1-0.5 mdyne/Å,[14,15] is such that gross disagreement between the empirical and diatomic force constants can be taken as evidence that the frequencies used to calculate the latter actually represent mixed modes or as evidence of incorrect assignments.

Table I summarizes the bond distance data, the assigned vibrational frequencies, and the empirical and diatomic force constants of the $Re_2X_8^{2-}$ series (X = F, Cl, Br). The RR data are from solid-state and solution studies by earlier workers[5,7,11] confirmed by results from our laboratories.[6] The RR assignments are from the earlier studies.[5,7] The empirical and diatomic force constants correspond well for the chloride and bromide complexes, supporting the previous assignments and suggesting relatively little mixing of internal coordinates in these systems. In the fluoride complex, however, the agreement between the empirical and diatomic force constants is poor for both the Re-Re stretch and the Re-F stretch. The strong enhancement in $\delta\delta^*$ resonance and the overtone progressions of the 318-cm^{-1} vibration of $Re_2F_8^{2-}$[5] leave no doubt that the assignment of this peak as primarily the Re-Re stretching mode is correct. Accordingly, the poor agreement between the diatomic and empirical force constants is probably due to mixing of the Re-Re coordinate with the Re-Re-F deformation which should appear near 200 cm^{-1} in the fluoride and could thereby be responsible for an apparently high Re-Re frequency.

The assignment of the Re-F stretching mode is more difficult to establish. The earlier assignment[5,7] of the Re-F stretch is to the weak peak at 623 cm^{-1}; however, other weak features may be equally valid candidates. A specific possibility is the peak at 502 cm^{-1} which was previously assigned as a combination. Its frequency is 3 cm^{-1} too high to be the harmonic frequency of the assigned combination (318 + 181 cm^{-1}), while all of the other combination frequencies are (as expected) lower than the harmonic sums. The frequency calculated for the Re-F stretch based upon the empirically estimated force constant of the Re-F bond (Table I) is 572 cm^{-1}, almost equidistant from 623 cm^{-1} and 502 cm^{-1}, and therefore the empirical rules are not very informative as to this assignment. It is clear, however, that coordinate mixing is a factor in this motion as well as in the Re-Re stretch. It is reasonable to suggest that the 181-cm^{-1} peak represents the Re-Re-F deformation. Quantitative formal vibrational analysis of these systems as well as analysis of their RR intensities and concomitant vibrational dynamics is required to resolve these questions and is proceeding in these laboratories.

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Organic Reactions in Liquid Crystalline Solvents. 6. Regiochemical Control of Bimolecular Chemical Reactivity in Smectic and Cholesteric Liquid Crystals

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There has been considerable recent interest in the potential ability of liquid crystalline solvents to affect bimolecular chemical reactivity as a result of controlling the orientation of reactants or exerting special effects on transition-state dynamics.[2-6] The studies that have been carried out, along with various others directed toward probing the effects of these media on unimolecular solute reactivity and conformational mobility,[7-12] have led to the general view that the molecular ordering present in nematic and cholesteric liquid crystals is not sufficiently rigid to alter the reactivity of dissolved solutes significantly; most "successful" studies have employed smectic phases, which are considerably more rigidly ordered than simple nematics or cholesterics.[13] We now

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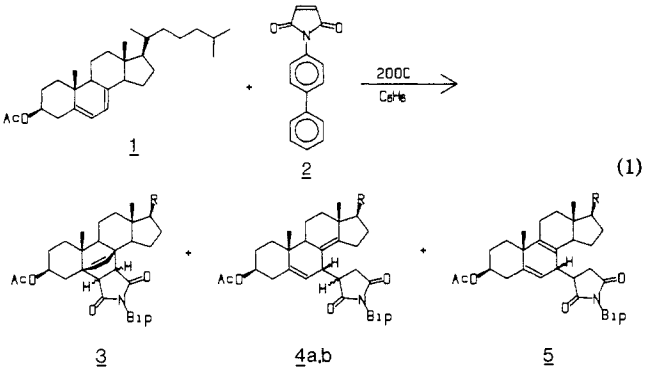
Table I. Product Yields from Reaction of **1** and **2** in Isotropic and Liquid Crystalline Solvents at 200 °C[a]

solvent	3 + 4b	4a	5	?[b]	transition temps[c] (°C) pure	transition temps[c] (°C) doped[d]
benzene (I)	48[e]	31	14	6		
S1409 (I)	43	31	19	8	147–147.5 (S–N) 165–165.5 (N–I)	141–147 (S–N) 162–163 (N–I)
cholestanyl benzoate (I)	43	31	17	9	137–139 (K–Ch) 155–157 (Ch–I)	134–136 (K–Ch) 151–153 (Ch–I)
cholesteryl-4-chlorobenzoate (C)	29	25	32	13	170–171.5 (K–Ch) 248.5–250 (Ch–I)	164–171 (K–Ch) 247–249 (Ch–I)
S1544 (Sm B)	28	24	39	9	234–236 (S–S) 256–257 (S–N)	229–232 (S–S) 244–256 (S–N)

[a] As 1.5 wt% or 0.03 M deoxygenated solutions (equimolar **1** and **2**) in sealed tubes. Yields were determined by analytical HPLC (silica gel, 280 nm) analysis;[17a] errors are estimated to be ±10%. Adducts **3** and **4b** elute together under these conditions. [b] Not yet identified. [c] Measured by thermal microscopy; corrected. K = crystalline, Sm = smectic, Ch = cholesteric, N = nematic, I = isotropic. [d] With 0.9 wt% **1** and 0.6 wt% **2**. [e] The relative yields of **3** and **4b** from the reaction in benzene are **3**:**4b** = 2.7 ± 0.7; as determined by C18 reverse phase HPLC analysis of the mixture isolated by preparative silica gel HPLC.[17a,b]

wish to report results that demonstrate the potential of these weakly ordered phases to alter the course of bimolecular reactivity, providing the first example of the use of liquid crystalline solvents to "steer" the reactivity of two solutes in favor of products whose transition states are most compatible with the weakly ordered, local solvent matrix.

Cholesta-5,7-dien-3β-yl acetate (**1**) and other steroidal dienes are known to undergo ene and Diels–Alder cycloadditions with a number of electrophiles.[14] Similarly, reaction of **1** with *N*-biphenylmaleimide[15] (**2**) in benzene solution at 200 °C for 4 h affords the mixture of Diels–Alder and ene adducts shown in eq 1. The products were isolated by semipreparative medium



1 2 (1)

3 4a,b 5

pressure chromatography,[16a] and their structures were assigned on the basis of IR, mass, and ^{13}C and ^{1}H NMR spectroscopy[16b] and by analogy with the spectra of the corresponding ene adducts from reaction of **1** with dimethyl diazodicarboxylate (DMDD)[14a] and dimethyl acetylenedicarboxylate (DMAD)[14b] and those of the Diels–Alder adducts of ergosterol derivatives and *N*-phenyltriazolinedione.[14c] Product yields were determined by HPLC analysis of the crude reaction mixtures[17a] and were identical with those determined after shorter heating periods when the reaction was less than ca. 40% complete. Each adduct was found to be stable to prolonged heating at 200 °C.

The reaction of equimolar mixtures of **1** and **2** as 1.5 (total) wt% solutions in the cholesteric and isotropic phases of two steroidal esters, the smectic phase of 4-(*trans*-pentylcyclohexyl)-4′-(propylcyclohexyl)biphenyl (S1544), and the isotropic phase of another mesogenic alkylbiphenyl derivative (S1409) under similar conditions to those used above afforded the same products as observed in benzene, in the yields summarized in Table I.[17a,b] No new products, formed in addition to those shown in eq 1, were observed in any case. Table I also shows transition temperatures for the various mesogens and their mixtures with the reactants, measured by thermal microscopy.

Within the series of steroidal, aromatic, and mixed steroid–aromatic[17c] isotropic solvents collected in Table I, it is clear that (as expected) there is very little, if any, bulk solvent effect on the relative yields of the various products obtained from reaction of **1** and **2**, in spite of considerable differences in solvent polarity, polarizability, and viscosity within the series. In each of the liquid crystalline phases examined the yield of *one* of the products (**5**) is clearly enhanced relative to those of the others and to an extent that appears to be roughly independent of mesophase type.[18]

We explain the enhancement in the relative yield of **5** that occurs in cholesteric solvents by considering the required relative orientations of the two reactants in the transition states for formation of the various products. These are shown in Scheme I for the ene adducts **4** and **5**. Formation of **4** (as well as the Diels–Alder adduct) must occur via a transition state in which

(13) (a) On the molecular level, the short-range order present in cholesteric liquid crystals is very similar to that in simple nematics.[13b] (b) *Liquid Crystals. The Fourth State of Matter*; Saeva, F. D., Ed.; Marcel Dekker, Inc.: New York, 1979.

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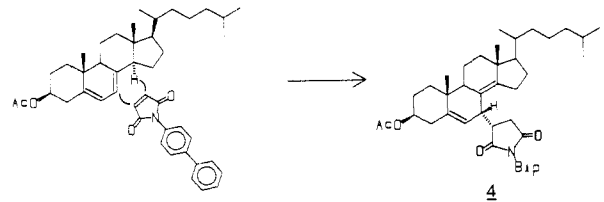
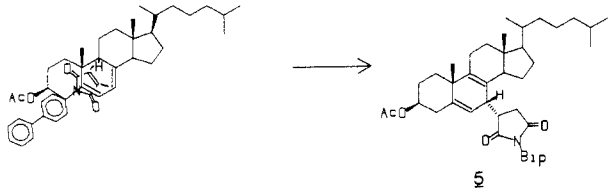
(16) (a) The products were separated, after evaporation of the solvent, by cyclic medium pressure chromatography,[11d] employing a 31 × 2.5 cm silica (40–60 μm) column, acetonitrile (2%)/dichloromethane as eluant, and an 8 mL/min flow rate. Adducts **5**, **4a**, and a mixture of **3** and **4b** were isolated as single peaks (in order of elution) after 3 cycles through the column. The fifth adduct, which eluted last, has not yet been obtained in sufficient quantities to enable identification. Adducts **3** and **4b** were separated from their mixture by preparative reverse phase HPLC, by using a 25 × 2.5 cm C18 column with acetonitrile as eluant. Each adduct was then chromatographed a second time and finally recrystallized from methanol to yield colorless solids with melting points as follows: **3**, 119–121 °C; **4a**, 95–97 °C; **4b**, 120–123 °C; **5**, 130–132 °C. (b) Structural assignments for **4a,b** and **5** have been made primarily on the basis of ^{1}H NMR evidence, by analogy with the corresponding **1**-DMDD[14a] and **1**-DMAD[14b] ene adducts, and by comparison of the ^{13}C NMR spectra to that of **1**[16c] (carbons 9 and 14, in particular). The ^{1}H NMR assignment is made on the basis of the chemical shifts due to the methyl groups corresponding to carbons 18 and 19. The adducts assigned as **4a** and **4b** each show two methyl singlets, separated by ca. 0.01 ppm, around 0.90 ppm, while the adduct assigned as **5** shows two methyl singlets at 1.20 and 0.64 ppm. These correspond almost exactly to the chemical shifts for these methyl protons in the corresponding **1**-DMAD adducts.[14b] The isomeric identities of **4a** and **4b** have not yet been fully established nor has that of the Diels–Alder adduct **3**. The latter product exhibits two vinyl proton resonances at 6.24 and 5.83 ppm. ^{1}H and ^{13}C NMR data for **3**–**5** are available as Supplementary Material; full experimental details will be published in the full paper. (c) Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic Press: New York, 1972.

(17) (a) Product yields were determined by analytical HPLC,[11d] by using a silica gel column (10 μm; 0.47 × 25 cm; acetonitrile (10%)/dichloromethane), with detection by UV absorption (280 nm). The detector was not calibrated with respect to possible variations in response factors. Peak areas were calculated by triangulation and/or the cut and weigh method. (b) Product yields for **3** and **4b** have been reported in Table I as the sum, since these are the most accurate data available to us. Determination of the actual composition of the mixture of the two products requires isolation of the mixture and further analysis by reverse phase HPLC and is thus subject to substantially greater error. Preliminary analyses of this type indicate that the relative yields of **3** and **4b** do not vary appreciably throughout the series of solvents studied. (c) Several other steroidal solvents have been investigated in addition to those listed in Table I, including cholesteryl propionate (isotropic) and 4-anisoate (cholesteric), cholestanyl toluate (cholesteric), 5:2 cholestanyl toluate/toluene (isot), and 5:2 cholesteryl 4-chlorobenzoate/chlorobenzene (isotropic). The relative product yields in each of these cholesteric and isotropic solvents were similar to those observed in cholesteryl-4-chlorobenzoate and cholestanyl benzoate, respectively.

Scheme I



4



5

the two reactants are aligned with their long axes perpendicular to one another,[19] while formation of **5** requires a parallel relative orientation. Given the known ability of liquid crystals to orient dissolved solutes in a manner and to an extent that depends primarily on the structural similarities between the solute and the mesogen,[13b,20] it is expected that **1** and **2** will have preferred parallel relative orientations in the mesophase. The observed enhancement in the relative yield of **5** is proposed to result from a relative destabilization of those transition states that require considerable deviation of the reactants from their favored relative orientations in the ordered solvent. The extent to which such alterations in relative product yields will occur should depend on a number of factors, such as the extent to which the reactants themselves disrupt local solvent order, the lengths and flexibilities of the reactants, and the interplay between the ordered solvent's effects on the activation enthalpy (which should favor "parallel transition states") and entropy (which should favor "perpendicular" ones).[3d,10,11]

Given the much greater degree of order and rigidity associated with smectic B phases compared to cholesterics and nematics,[13,20] the similarity in the effects of the cholesteric and smectic (S1544) solvents on the product distribution may be surprising. This is apparently not due to poor solubility of the reactants in the smectic phase (leading to solubilization and subsequent reaction primarily in a solute-rich nematic phase),[11d] since thermal microscopic inspection of variously proportioned mixtures of **1** and S1544 (1–5 wt%) indicates uniform solubility over the entire Sm B temperature range, even at the 5 wt% level. The relatively small effect of the smectic phase on the reaction may be the result of the reactive solutes' immediate environment being somewhat disordered, which is reasonable considering the substantial differences in the structures of **1** and the smectogen.[21a] Microscopic solvation effects of this type have been proposed previously in other related studies[2,4,10,11] and are substantiated by thermodynamic data.[20e]

By the same token, local solvent order in the cholesteric phases should be only slightly disrupted by the presence of **1**, so that the potential effect of this phase type on the reactivity of **1** is maximized. These factors are reflected macroscopically in the effects of solute incorporation on the transition temperatures of the pure mesogens (see Table I).

We are continuing our investigations of this system to examine the extent to which the ability of various liquid crystalline phases to control reactivity in this fashion depends on mesophase type and reactant length and flexibility.

Acknowledgment. We thank E. Merck (Darmstadt) for generous supplies of S1544 and S1409 and Dr. D. Hughes (McMaster University) for acquiring the high field NMR spectra. Financial support for this work was provided by the Research Corporation and the Natural Sciences and Engineering Research Council of Canada.

Supplementary Material Available: ^1H and ^{13}C NMR spectra for **3**, **4a**, **4b**, and **5** (9 pages). Ordering information is given on any current masthead page.

(18) Adduct **5** has been isolated from runs in several of the cholesteric and isotropic solvents employed and has been shown to consist of only a single component by HPLC analyses under several different sets of conditions.

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(21) (a) Alternatively, the result may indicate that reaction of **1** and **2** takes place primarily in the relatively fluid, interlayer region of the smectic phase, as has been suggested previously to explain the behavior of other probe molecules in Sm B phases,[3e,8,21b,c] although we have no real evidence to support this suggestion. (b) Lin, W.; Freed, J. H. *J. Phys. Chem.* **1979**, *83*, 379. (c) Meirovitch, E.; Ignere, D.; Ignere, E.; Moro, G.; Freed, J. H. *J. Chem. Phys.* **1982**, *77*, 3915.

Radical Intermediates in the Epoxidation of Alkenes by Cytochrome P-450 Model Systems. The Design of a Hypersensitive Radical Probe

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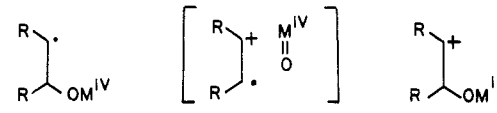
The cyclopropylcarbinyl to homoallylcarbinyl radical rearrangement (CPCRR) has been used as a trap for radical intermediates in enzymic[1] and nonenzymic[2] reactions. Radical and cationic intermediates proposed[3] for the epoxidation of alkenes by metalloporphyrin model and cytochrome P-450 systems are



1 2 3

We report preliminary observations on the use of the *trans*-2,-*trans*-3-diphenylcyclopropyl substituent as a trap for intermediates **1** and **2**. The synthetic procedures for preparing compounds **4**-Z, **4**-E, **5**-t, **5**-c, **6**, **8**, and **9** required for this study, along with full structural characterizations (elemental analysis, mass spectroscopy, H^1 NMR and FT-IR) will be given in the full report.

Epoxidation of **4**-Z with $(F_{20}TPP)Fe^{III}(Cl)$[4] and C_6F_5IO (CH_2Cl_2 solvent, under N_2) provided **5**-c in 92–95% yield based on reacted **4**-Z. Neither **4**-E nor **5**-t are present as ≥0.1% (detection limit) of the reaction products. These stereoisomerization products would result from carbon–carbon bond rotation in **1**, **2**,

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(4) The abbreviation $(F_{20}TPP)Fe^{III}(Cl)$ is for 5,10,15,20-*meso*-tetrakis-(pentafluorophenyl)porphinatoiron(III) chloride.

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