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(3) Photochemical isomerization **2** → **1** was unobserved both at 350 and 254 nm.
(4) The isomerization **1** → **2** was driven on a small scale cleanly but slowly likewise to >99% conversion by Pyrex filtered direct December sunlight (Boston, Mass.).
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Conformational Control by Carbinyl Hydrogens. Implications and Applications

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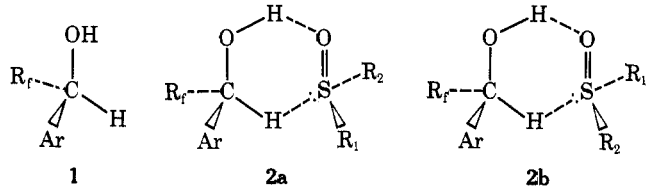
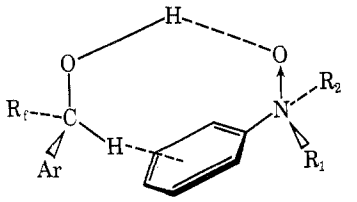
"Acylation shifts" and Eu(fod)$_3$ gradients of the carbinyl hydrogens of a variety of esterlike derivatives of secondary alcohols are substantially enhanced when the carbinyl carbon bears a trifluoromethyl group. This enhancement is not steric in origin and is attributed to weak intramolecular bonding between the carbinyl hydrogen and the carbonyl oxygen which populates conformations placing the carbinyl hydrogen near to and approximately in the plane of the magnetically anisotropic carbonyl. Here, this hydrogen may be deshielded (acylation shift) or shifted downfield (gradient) upon coordination of the carbonyl oxygen to Eu(fod)$_3$. The concept of conformational control by carbinyl hydrogen bonding can be used to account for prior instances of chemical behavior such as chromatographic properties, NMR chemical shifts, and asymmetric induction.

Prior papers dealing with chiral NMR solvents have explained the ability of these solvating agents to cause the spectra of enantiotopic solutes to become nonequivalent as a consequence of the formation of transient diastereomeric solvates.[1-6] Further, it has been proposed that these solvates assume conformations which place enantiomeric solute nuclei in different orientations with respect to a magnetically anisotropic substituent of the chiral solvating agent. Accurate knowledge of the conformational behavior of these diastereomeric solvates would enable one to directly relate the observed spectral differences to the stereochemical differences of the solvates.[7] For chiral solvents of known absolute configuration, this type of spectral interpretation would amount to *simultaneous determination of the absolute configuration and enantiomeric purity of the solute*. Clearly, an understanding of the factors underlying the conformational behavior of the transient diastereomeric solvates is essential to the successful employment of this technique.

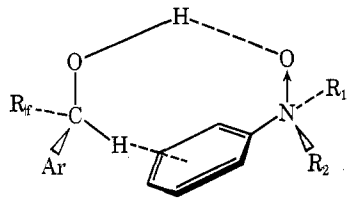
Specific solvation models have been advanced[1,2] to account for the NMR nonequivalence shown by enantiomeric sulfoxides or enantiomeric tertiary amine oxides in the presence of chiral type 1 alcohols. After initial intermolecular hydrogen bonding, a weaker but intramolecular bonding between the carbinyl hydrogen of 1 and a second basic site in the solute is postulated to afford chelatelike conformations exemplified by **2a,b** and **3a,b**. Such conformations would place enantiomeric solute nuclei (R_1 or R_2) in different orientations with respect to the aromatic substituent of chiral alcohol 1. Hence, the resultant average chemical shift



1 2a 2b



3a



3b

differences between solute enantiomers stem from differential shielding effects in the diastereomeric solvates and are easily relatable to solute stereochemistry.

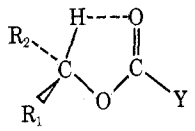
While the ability of the hydroxyl of a type 1 alcohol to hydrogen bond to basic solutes is easily demonstrated, the ability of the carbinyl hydrogen of 1 to exert a secondary bonding interaction on weakly basic sites such as π electrons or unshared electron pairs is less obvious. The question of the existence of this latter type of bonding is a rather important one, for the conformational control proposed to result thereby does account for the occurrence of enantiomeric spectral nonequivalence and does correctly correlate the senses of this nonequivalence with the absolute configurations of a wide variety of solute classes, these models not being restricted solely to sulfoxides or amine oxides.[12] Inasmuch as the determination of absolute configuration is a frequently encountered problem, the development of a convenient, reliable, easily understood method for simultaneously determining absolute configuration and enantiomeric purity would be quite useful. For this reason, we have investigated several systems where such weak intramolecular bondings might result in demonstrable conformational control, an observation which would have considerable bearing upon the merits of the proposed solvation models.

In the case of esterlike derivatives of type 1 alcohols, weak intramolecular bonding between the carbinyl hydrogen and the carbonyl oxygen would be quite analogous to the previously postulated chelating interactions and should exert some degree of conformational control.

There are two reasons to anticipate this conformational control. First, the case for *intermolecular* hydrogen bonding between chloroform and several bases has been reviewed by Pimentel and McClelland and judged to be sound.[13] Equally relevant, evidence for the *intermolecular* hydrogen bonding of chloroform to the π cloud of benzene has been offered.[14] Secondly, the $T\Delta S$ term for *intramolecular* hydrogen bonding is essentially zero, whereas it has been estimated to be ca. 3 kcal/mol for *intermolecular* hydrogen bonding in solution.[15] Thus, a weak bonding interaction of a given enthalpy will be rather more effective in controlling conformation populations in the *intramolecular* case than in controlling extent of association in the *intermolecular* case.

In a sense, the carbinyl hydrogen of 1 is analogous to the methine hydrogen of chloroform in that both have three inductively electron-withdrawing groups in the α position. To the extent that the "acidity" of the carbinyl hydrogen plays a role in the postulated CHB, the presence or absence of the electronegative trifluoromethyl group should have predictable consequences in terms of the extent of conformational control arising through CHB.

Several years ago, the acylation shift undergone by carbinyl hydrogen resonances upon acylation of alcohols was related by Culvenor[16] to the population of conformers similar to 4 which place the carbinyl hydrogen in or near the



4

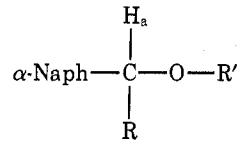
plane of the magnetically anisotropic acyl carbonyl group. Culvenor offers no forthright explanation as to the reasons underlying the population of conformer 4, although it was known at that time from microwave data that the methoxyls of methyl formate and methyl acetate are cis to carbonyl oxygen but ca. 25° out of the carbonyl plane.[17] X-ray data for several crystalline esters also indicates close approach (2.22 Å) of the carbinyl hydrogen to carbonyl oxygen in the solid state.[18] Conformations approximating 4 have been used by Karger[19] and Helmchen[10] to account for the elution order of diastereomeric esters and amides upon gas and thin layer chromatography. Almost invariably, the reasons for the population of conformers like 4 are assumed to be steric or else not mentioned at all. An exception to this is Mathieson, who contemplated, on the basis of his x-ray work, the possible existence of a weak intramolecular bonding force between the carbinyl hydrogen and carbonyl oxygen of an ester.[18] However, Mathieson concluded that "repulsive forces" are dominant in determining ester conformation although "subsidiary local forces" play a role as well. If real, CHB could play a substantial role in populating conformations like 4.

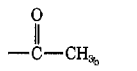
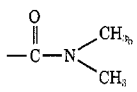
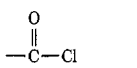
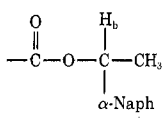
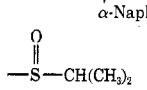
Results and Discussion

On steric grounds, the conformational behavior of 1,1,1-trifluoro-2-propyl acetate (6) is expected to be intermediate between that of 2-propyl acetate (7) and 3,3-dimethyl-2-butyl acetate (8), since the van der Waals diameter of the trifluoromethyl group (5.1 Å) is intermediate between that of methyl (4.0 Å) and *tert*-butyl (6.2 Å). If steric effects alone are responsible for population of conformations like 4, then the acetylation shifts are expected to occur in the order 7 < 6 < 8. However, if the presence of the trifluoromethyl group in 6 results in increased population of conformations like 4, a greater acetylation shift would be observed for the fluoro alcohol than for the other two alcohols.[20] In actuality, the acetylation shift of 1,1,1-trifluoro-2-propanol is 1.48 ppm vs. 1.25 ppm for 2-propanol and 1.20 ppm for 3,3-dimethyl-2-butanol. Similar arguments apply to the *N,N*-dimethyl carbamates of these three alcohols, but, again, the fluoro alcohol undergoes the greater (1.10 vs. 0.80 and 1.06 ppm) "acylation shift".

Further studies were conducted on 2,2,2-trifluoro-1-(1-naphthyl)ethanol[22] (10) (of interest as a chiral NMR additive for determining absolute configurations and enantiomeric purities[1]) and its nonfluorinated analogues, 1-(1-naphthyl)ethanol (11) and 2,2-dimethyl-1-(1-naphthyl)-propanol (12). Conversion of these alcohols respectively into acetates, **13a–c**, *N,N*-dimethyl carbamates, **14a–c**, chloroformates, **15a,b**, or carbonate **16**[23] results in a greater "acylation shift" for fluoro alcohol **10** than for alcohols **11** or **12** (see Table I). This result is consistent with the view that trifluoromethyl group more heavily populates conformations which place the carbinyl hydrogen near the deshielding carbonyl oxygen. It is obvious that these greater acylation shifts do not stem solely from steric origins, since trifluoromethyl is intermediate in size between methyl and *tert*-butyl. Only in the case of the sulfinates **17a,b**,[23] derived from reaction of **10** and **11** with 2-propylsulfinyl chlo-

Table I. Carbinyl Hydrogen "Acylation Shifts" and Eu(fod)$_3$ Gradients of Some Alcohol Derivatives



Compd	R′	R	Acylation shift H_a, ppm[a]	Eu(fod)$_3$ H_a, ppm	Gradient[b] H_b, ppm
13a–c		CF_3	1.33	9.4	6.4
		CH_3	1.15	5.9	7.4
		$C(CH_3)_3$	1.15	6.7	7.0
14a–c		CF_3	1.30	17.	8.7
		CH_3	1.05	11.	12.
		$C(CH_3)_3$	1.05	13.	10.
15a,b		CF_3	1.28		
		CH_3	1.00		
16		CF_3	1.20 (H_a) 1.05 (H_b)	2.6	0.8
17a,b		CF_3	0.58	19.	
		CH_3	0.55	10.	

[a] Chemical shifts were obtained for quite dilute carbon tetrachloride solutions at 28 °C. [b] Gradients are presented as least-squares slopes of the essentially linear portion of the curves noted for Eu(fod)$_3$: substrate ratios of less than 0.2. The correlation coefficients of the least-squares slopes range from 0.99 to 0.97.

ride, are the acylation shifts similar. By the preceding criteria, one might conclude that there is no significant difference in the conformational behavior of these sulfinates. Data to be subsequently presented make this seem unlikely, and it is tentatively concluded that the asymmetric magnetic anisotropy about the sulfinyl group coincidentally occasions the similar "acylation" shifts. A relevant observation here is that the preferred conformation of thiacyclohexane 1-oxides places the sulfinyl oxygen in an axial position.[24,25] It has been suggested[24,25] and supported[26] by calculations that there is an attractive interaction between the axial oxygen and the axial γ hydrogens amounting to 0.37 kcal/mol, even though the γ hydrogens would not be expected to be especially acidic.

Lanthanide Shift Studies. Independent supportive evidence for the ability of an α-trifluoromethyl group to preferentially populate type **4** conformations comes from a study of the effect of Eu(fod)$_3$ upon the chemical shifts of the carbinyl hydrogens of the aforementioned derivatives of alcohols **10, 11,** and **12.** Eu(fod)$_3$ is known to coordinate to the carbonyl oxygen in a variety of carbonyl containing compounds. While thus coordinated, it exerts a deshielding influence on nearby protons which diminishes with increasing distance from the lanthanide. The effect of Eu(fod)$_3$ concentration upon the chemical shifts of the carbinyl hydrogen and acetyl methyl resonances of dilute carbon tetrachloride solutions of acetates **13a–c** was determined. At low ratios of Eu(fod)$_3$/substrate, these plots are essentially straight lines, the least-squares slopes of which are given in Table I. If one uses the slope (gradient) of the acetyl methyls as an index of the extent of coordination by the Eu(fod)$_3$, one infers that acetates **13b,c** coordinate more strongly than fluorinated acetate **13a.** This is expected a priori since the electron-withdrawing trifluoromethyl should reduce the basicity of the carbonyl oxygen of **13a** relative to **13b,c.** Nevertheless, the gradient for the carbinyl hydrogen of fluoroacetate **13a** is greater than those of **13b** or **13c** even before allowance is made for **13a**'s reduced degree of coordination. Competition experiments between equal concentrations of **13a** and **13b** show that Eu(fod)$_3$ coordinates preferentially to **13b** by a factor of ca. 7:1. Judging from the acetyl methyl gradients, the more hindered **13c** is complexed to a slightly lesser degree than **13b.** However, from the carbinyl hydrogen gradients, the additional steric bulk appears to favor conformations placing the carbinyl hydrogen near the lanthanide while complexed.

Other data in Table I show that the rates at which the carbinyl hydrogens are shifted downfield by Eu(fod)$_3$ addition varies from derivative to derivative as changes in the basicities of the carbonyl oxygens influence the extent of coordination to Eu(fod)$_3$. For example, the carbonate **16** appears to coordinate more weakly than any of the carbamates. Note however, that within a class, the carbinyl hydrogen of the derivative of fluoro alcohol **10** is shifted more strongly than that derived from **11** or **12** *despite the fact that the carbonyl basicities of the derivatives of* **10** *must be less than those of* **11** *or* **12.** As further illustration of this point, note that the *N*-methyl group cis to the carbonyl oxygen in *N,N*-dimethyl carbamate **14a** (derived from fluoro alcohol **10**) is not shifted downfield as strongly as those in carbamates **14b** and **14c,** derived from **11** and **12.** A competition experiment employing equal concentrations of **14a** and **14b** shows that Eu(fod)$_3$ preferentially coordinates to **14b** by a 3:1 margin. Use of the mixed carbonate **16** avoids problems of differing extents of coordination to Eu(fod)$_3$ since both types of carbinyl hydrogens are present in the same molecule. Again, it is the carbinyl hydrogen derived from **10** which is most strongly influenced by the addition of Eu(fod)$_3$, the initial slope of its $\Delta\delta$ vs. Eu(fod)$_3$ curve being over twice that of its less acidic partner. Finally, despite probable basicity differences, the greater Eu(fod)$_3$ gradient of the carbinyl hydrogen of fluoro alcohol **10** is especially evident for sulfinates **17a** and **17b** which, it may be recalled, show no difference in their "acylation" shifts.

The preceding results clearly indicate that the carbinyl

hydrogens of the derivatives of fluoro alcohol **10** are, on the average, closer to the complexed Eu(fod)$_3$ than their counterparts in the derivatives of **11** and **12**. Again, this is most readily explained in terms of a weak bonding between the carbinyl hydrogen and the carbonyl oxygen. The strength of this interaction would appear to increase with increased "acidity" of the carbinyl hydrogen. Presumably, the carbonyl (or sulfinyl) oxygen retains some basic character during coordination to Eu(fod)$_3$ and still serves as an acceptor for CHB.[27] While one must not be unmindful of the ability of shift reagents to influence conformational equilibria,[28] it seems reasonable that CHB in the uncoordinated derivative would be even stronger.

The preceding data clearly demonstrate that the α-trifluoromethyl group plays a substantial role in preferentially populating type 4 conformations of esterlike derivatives of type 1 alcohols. This demonstration is of considerable importance, since it furnishes analogy for the conformations, **2a,b, 3a,b,** invoked to account for the ability of chiral type 1 alcohols to promote ^{1}H NMR spectral nonequivalence for enantiomeric sulfoxides and amine oxides. This analogy does not hinge upon the correctness of the rationale (i.e., CHB) for the reason underlying the population of these conformations, although this too is important in that real understanding of the origin of the conformational preference might suggest structural modifications which would further bias this conformational preference.

The results of Karger et al.[29] on the correlation of stereochemistry with gas chromatographic elution order of diastereomeric esters of secondary alcohols can be rationalized on the basis of preferred conformations in which the carbinyl hydrogen is in or near the plane of the carbonyl group. Similar conformations have been used by Helmchen et al.[10] in correlating stereochemistry with chromatographic and NMR behavior of some diastereomeric amides and by Moser et al.[8,9] in correlating stereochemistry and ^{1}H NMR spectral differences between diastereomeric esters of secondary alcohols.

It is suggested that carbinyl hydrogen bonding may play an active role in causing the population of the aforementioned conformers and may also manifest itself during some asymmetric induction reactions.

Experimental Section

Melting points were determined on a Büchi apparatus and are uncorrected. Proton NMR spectra were obtained with Varian Associates A-60A, A56-60, or HA-100 instruments. Infrared spectra were obtained with a Beckman IR-12. Mass spectra were determined using a Varian MAT CH-5 spectrometer. Microanalyses were performed by J. Nemeth and his colleagues.

Acetates. All of the acetates used in this study were prepared using the following procedure. Acetyl chloride (0.517 g, 6.63 mmol) was added via syringe to a cold (−78°C) solution of racemic alcohol (ca. 4.5 mmol) and triethylamine (0.67 g, 6.6 mmol) in 30 ml of fluorotrichloromethane. After 15 min, the amine hydrochloride was removed, the solvent evaporated, and the crude acetate molecularly distilled. In some instances, the acetates were purified by chromatography on silica gel with methylene chloride using a system similar to that described.[30]

1-(1-Naphthyl)-2,2,2-trifluoroethyl acetate (13a) was an oil (95% yield): NMR (CCl_4) δ 2.13 (s, C–CH_3), 6.95 (quartet, CH), 7.30–8.15 ppm (multiplet, $C_{10}H_7$); ir (neat) 3090, 2970, 1760 (C=O), 1370, 1270, 1215, 1135, 1065 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 268 (69.05, M$^+$), 225 (4.5), 209 (12.5), 157 (100).

1-(1-Naphthyl)ethyl acetate (13b) was an oil (>95% yield): NMR (CCl_4) δ 1.6 (d, C–CH_3), 1.97 (s, C–CH_3), 6.55 (quartet, CH), 7.15–8.10 ppm (multiplet, $C_{10}H_7$); ir (neat) 3090, 3000, 1745 (C=O), 1450, 1360, 1250, 1175, 1110 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 214 (61.99, M$^+$), 172 (37.38), 155 (91.86), 154 (99), 128 (34).

1-(1-Naphthyl)-2,2-dimethylpropyl acetate (13c) was a yellow oil (85% yield): NMR (CCl_4) δ 0.96 [singlet, C(CH_3)$_3$], 2.00 [singlet, C(=O)CH_3], 6.45 (singlet, CH), 7.30–8.20 ppm (multiplet, $C_{10}H_7$); ir (neat) 3060, 2990, 1750, 1640, 1550, 1370, 1350, 1120 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 256 (11.70, M$^+$), 199 (22.53), 157 (100), 129 (21.86), 127 (7.80).

Carbamates. All of the carbamates used in this study were made by the following procedure. Sodium hydride–mineral oil dispersion (5.0 mmol) was added to the alcohol (ca. 4.5 mmol) in 10 ml of dry tetrahydrofuran. When gas evolution ceased, *N,N*-dimethylcarbamoyl chloride (0.60 g, 5.6 mmol) was added in small portions. After 15 min, 100 ml of water was added and the solution was extracted twice with 25-ml portions of methylene chloride. The dried extracts were concentrated and the residual material chromatographed on silica gel with methylene chloride using a system similar to that described.[30]

1-(1-Naphthyl)-2,2,2-trifluoroethyl-*N,N*-dimethyl carbamate (14a) was straw-colored crystals (90% yield): mp 65.6–66.2; NMR (CCl_4) δ 2.91 (broad s, NCH_3), 6.94 (quartet, CH), 7.32–8.14 ppm (multiplet, $C_{10}H_7$); ir (KBr) 3000, 2070, 1740 (C=O), 1410, 1578, 1190, 1100 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 297 (35.7, M$^+$), 209 (100), 159 (26.5), 121 (100).

Anal. Calcd for $C_{15}H_{14}F_3NO_2$: C, 60.89; H, 4.73; N, 4.73. Found: C, 61.35; H, 4.74; N, 4.80.

1-(1-Naphthyl)ethyl-*N,N*-dimethyl carbamate (14b) was an oil (>90% yield): NMR (CCl_4) δ 1.69 (d, C–CH_3), 2.90 (s, NCH_3), 6.45 (quartet, CH), 7.3–8.1 ppm (multiplet, $C_{10}H_7$); ir (neat) 3050, 2970, 2900, 1705 (C=O), 1600, 1380 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 243 (95.09, M$^+$), 155 (100).

1-(1-Naphthyl)-2,2-dimethylpropyl-*N,N*-dimethyl carbamate (14c) was an oil (65% yield): NMR (CCl_4) δ 1.00 [singlet, C(CH_3)$_3$], 2.92 (broad singlet, NCH_3), 6.39 (singlet, CH), 7.3–8.2 ppm (multiplet, $C_{10}H_7$); ir (neat) 3050, 2990, 1710, 1625, 1390, 1370, 1190 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 285 (9.47, M$^+$), 228 (16.8), 127 (3.09), 72 (100).

Chloroformates. Chloroformates were prepared in a manner analogous to that used by Altner.[31]

1-(1-Naphthyl)-2,2,2-trifluoroethyl chloroformate (15a) was purified by gel permeation chromatography on Bio-Beads SX-12 with CH_2Cl_2, and was obtained as a yellow liquid (71% yield): NMR (CCl_4) δ 6.90 (quartet, CH), 7.2–8.1 ppm (multiplet, $C_{10}H_7$); ir (neat) 3075, 1775 (C=O), 1540, 1358, 1260, 1240, 1190, 1140 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 288 (76, M$^+$), 219 (26), 209 (100), 188 (35), 182 (45).

Anal. Calcd for $C_{13}H_8ClF_3O_2$: C, 54.30; H, 2.78; Cl, 12.15. Found: C, 54.36; H, 2.79; Cl, 12.20.

1-(1-Naphthyl)ethyl chloroformate (15b) was purified by gel permeation chromatography on Bio-Beads SX-12 with CH_2Cl_2, and was obtained as a yellow liquid (60% yield): NMR (CCl_4) δ 2.0 (d, C–CH_3), 6.40 (quartet, CH), 7.2–8.2 ppm (multiplet, $C_{10}H_7$); ir (neat) 3050, 2980, 1730 (C=O), 1510, 1445, 1380, 1275, 1220 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 192 (73), 191 (37), 190 (100, M − CO_2), 174 (35), 157 (24), 156 (100), 155 (100), 150 (78), 138 (46), 126 (99), 115 (67), 86 (11).

1-(1-Naphthyl)-2,2,2-trifluoroethyl 1′-(1′-Naphthyl)ethyl Carbonate (16). 1-(1-Naphthyl)-2,2,2-trifluoroethyl chloroformate (**15a**, 2 g, 6.95 mmol) and racemic 1-(1-naphthyl)ethanol (**11**, 1.19 g, 6.95 mmol) were dissolved in 50 ml of benzene. After addition of pyridine (0.549 g, 6.95 mmol), the reaction mixture was refluxed for 48 h. This mixture was then filtered and the filtrate was concentrated and chromatographed on a Bio-Bead SX-12 gel permeation column. The effluent was monitored at 280 nm. The first major fraction to be eluted was carbonate **15** (yield 40%): NMR (CCl_4) δ 1.98 (d, C–CH_3), 6.45 (quartet, CH_3C**H**), 6.82 (quartet, CF_3C**H**), 7.1–8.1 ppm (multiplet, $C_{20}H_{14}$); ir (neat) 3090, 3000, 1745 (C=O), 1450, 1400, 1380, 1270, 1250, 1140 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 424 (57.78, M$^+$), 173 (94.45), 172 (100), 129 (100), 128 (54).

Sulfinates. The sulfinate esters described in this paper were prepared following a procedure developed by Hoekstra.[32]

1-(1-Naphthyl)-2,2,2-trifluoroethyl 2-Propyl Sulfinate (17a). Racemic fluorocarbinol **10** (0.994 g, 4.39 mmol) and pyridine (0.372 ml, 0.365 g, 4.61 mmol) were dissolved in 6 ml of $CFCl_3$ in a serum-stopped flask and cooled to −78 °C. 2-Propylsulfinyl chloride (5.0 mmol) was then added via syringe and the reaction mixture was shaken for 15 min. The reaction mixture was chromatographed on silica gel with CH_2Cl_2. Recrystallization of the high R_f diastereomer from 1:1 CH_2Cl_2–hexane afforded colorless crystals: mp 61.5–64.5 °C; NMR (CCl_4) δ 1.22 (d, C–CH_3), 2.76 (septet, CH), 6.19 (quartet, CH), 7.25–8.15 ppm (multiplet, $C_{10}H_7$); ir (KBr) 3060, 2995, 1635, 1515, 1470, 1400, 1345, 1240, 1120 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 316 (3.22, M$^+$), 209 (100), 127 (12.33).

Anal. Calcd for $C_{15}H_{15}F_3O_2S$: C, 57.09; H, 4.70. Found: C, 57.10; H, 4.65.

Although the high R_f diastereomer was used for NMR studies, its carbinyl hydrogen has essentially the same chemical shift as that of the low R_f diastereomer: NMR (CCl_4) δ 1.19 (d, C–CH_3), 2.72 (septet, CH), 6.14 (quartet, CH), 7.25–8.15 ppm (multiplet, $C_{10}H_7$).

1-(1-Naphthyl)ethyl 2-Propyl Sulfinate (17b). An oily mixture of diastereomers was obtained, inseparable by chromatography on silica gel (>90% yield): NMR (CCl_4) δ 1.15 [d, $C(CH_3)_2$], 1.75 (d, C–CH_3), 2.58 (septet, CH), 5.92 (quartet, CH), 7.22–8.15 ppm (multiplet, $C_{10}H_7$); ir (neat) 3070, 2970, 1540, 1235, 1135, 1070 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 262 (14.87, M^+), 155 (96.74), 154 (100), 128 (100).

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Registry No.—**10,** 17556-44-4; **11,** 57605-95-5; **12,** 57573-88-3; **13a,** 57573-89-4; **13b,** 57573-90-7; **13c,** 57573-91-8; **14a,** 57573-92-9; **14b,** 57573-93-0; **14c,** 57573-94-1; **15a,** 57573-95-2; **15b,** 57573-96-3; **16,** 57573-97-4; **17a** diastereomer a, 57573-98-5; **17a** diastereomer b, 57573-99-6; **17b** diastereomer a, 57574-00-2; **17b** diastereomer b, 57574-01-3; acetyl chloride, 75-36-5; *N,N*-dimethylcarbamoyl chloride, 79-44-7.

References and Notes

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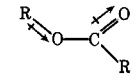
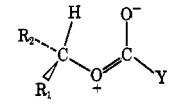
(20) An additional factor contributing toward the population of conformations placing ester alkoxyls cis to the carbonyl oxygen is likely to be simple antiparallel alignment of the bond dipoles associated with the C–O and C=O bonds as shown in **5**. This rationalization is similar to that used by



5

Bothner-By to explain why the methyl of propionaldehyde prefers to be cis to the carbonyl oxygen.[21] On the other hand, the electronegativity of the trifluoromethyl group will cause the ground-state basicities of both the alkoxyl and carbonyl oxygens of acetate **6** to be less than those of acetates **7** and **8**. Hence, the latter will be better able to support resonance as depicted in **9** and better able to serve as an intramolecular hydrogen bond acceptor. Moreover, the electronegativity of the trifluoromethyl group should also tend to diminish the magnitudes of the bond dipoles shown in **5** and hence possibly reduce the population of the cis conformer. On the basis of the latter three effects only, the acetylation shift of the fluoro alcohol would be expected to be *less* than that of the two other alcohols.



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(27) Coordination to $Eu(fod)_3$ will make the carbonyl oxygen a poorer receptor for CHB and some loss of CHB presumably results. This loss could conceivably be greater for the less acidic carbinyl hydrogens than for the more acidic carbinyl hydrogens and hence explain the substantially larger gradients of the latter.
(28) Since coordination to lanthanide makes the region about the carbonyl (sulfinyl) oxygen sterically more congested, one could conceivably preferentially populate the rotamer which places the smallest carbinyl substituent (i.e., the hydrogen) toward the lanthanide. Two aspects of this hypothesis worth contemplating are (a) the entire alkoxyl substituent could simply rotate away from lanthanide if steric interactions were too severe; (b) the carbinyl hydrogen gradients do not simply parallel the bulk of the alkyl substituent. The consequences of electronic interactions between the trifluoromethyl and the lanthanide shift reagent occurring in concert with steric forces cannot yet be predicted.
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