effect on the stereochemical consequences of the reaction of $(CH_3)_3SnLi$ with a *cis*- or *trans*-4-*tert*-butylcyclohexyl bromide; in fact, stereochemical equilibration still obtains in these reactions; however, a somewhat decreased preference for production of the trans isomer product is observed with inverse addition.[3b]

Second, a comparison of the reaction of $(CH_3)_3SnM$ and Ph_3SnM with optically active 2-octyl bromide reveals that, substitution with $(CH_3)_3SnM$ occurs readily at -20 °C while that with Ph_3SnM exhibits a comparable rate of reaction only when carried out at ambient temperature. However, while the reaction with $(CH_3)_3SnM$ can have a substantial free-radical component depending on various reaction parameters, the corresponding reaction with Ph_3SnM, whether carried out by normal or inverse addition, is essentially stereospecific. Thus

$$\underset{[\alpha]_D\ +38.6°}{(S)\text{-2-}C_8H_{17}Br} \xrightarrow[\text{THF, 25 °C}]{Ph_3SnLi} \underset{(c\ 4.15,\ C_6H_6)}{\underset{[\alpha]_D\ -23.3°}{(R)\text{-}\mathbf{2}}}$$

a significant kinetic distinction exists between free-radical and nonfree-radical pathways in this latter system.

Finally, these findings are relevant to the recently reported study of Kuivila and co-workers[7] who, using inverse addition conditions, concluded that >70% of the yield of **1**, resulting from the reaction of $(CH_3)_3SnNa$ with 2-octyl bromide in THF, is produced by pathways involving nongeminate free-radical combination. By contrast our studies reveal that under equivalent conditions, the reaction of $(CH_3)_3SnNa$ with 2-octyl bromide is highly stereoelective and can even be stereospecific, thereby *excluding* extensive participation of nongeminatge free-radical pathways. As the conclusions of these authors were based on the results of various trapping experiments, we conclude that the additives which were employed as trapping agents must be introducing a substantial perturbation on the mechanism of this reaction and, consequently, that such results cannot be considered as a reliable indication of those mechanisms that obtain in the absence of such reagents.

A Chiroptical Method for Determining the Absolute Configuration of Allylic Alcohols

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Received March 6, 1981

The circular dichroic exciton chirality method, a nonempirical method based on the coupled oscillator theory, has been successfully used in various organic compounds for the determination of absolute configurations.[1] As an extension of the exciton chirality method, we report a new CD method for determining the absolute stereochemistries of allylic alcohols.

The concept of chiral exciton coupling can be extended to nondegenerate systems composed of two different chromophores, e.g., the benzoate/enone system.[2] Allylic alcohol benzoates also give rise to a coupled nondegenerate system. Namely, the benzoate chromophore exhibits an allowed $\pi \rightarrow \pi^*$ intramolecular charge-transfer band at 230 nm, while the C–C double-bond chromophore also shows an allowed $\pi \rightarrow \pi^*$ transition around 195 nm;[3] both $\pi \rightarrow \pi^*$ transitions are polarized along the long axes of the chromophores. Therefore, the exciton theory predicts[4] that, if the two long axes of benzoate and double-bond chromosphores constitute a positive exciton chirality, i.e., right-handed screwness, the first Cotton effect at longer wavelengths (230-nm benzoate Cotton effect) is positive, while the second Cotton effect at shorter wavelengths (195-nm double bond $\pi \rightarrow \pi^*$ Cotton effect) is negative (Figure 1). On the other hand, if the allylic benzoate constitutes a negative exciton chirality, the 230-nm benzoate Cotton effect should be negative.

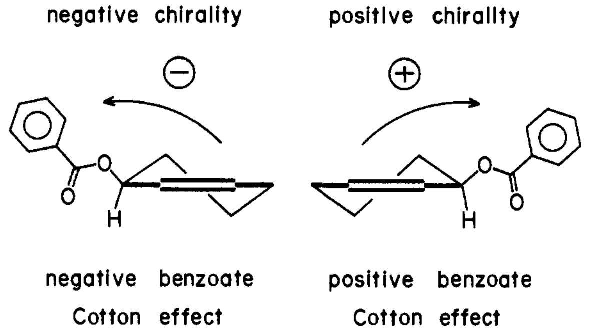

Figure 1. Exciton chirality of allylic benzoates and sign of benzoate Cotton effects.

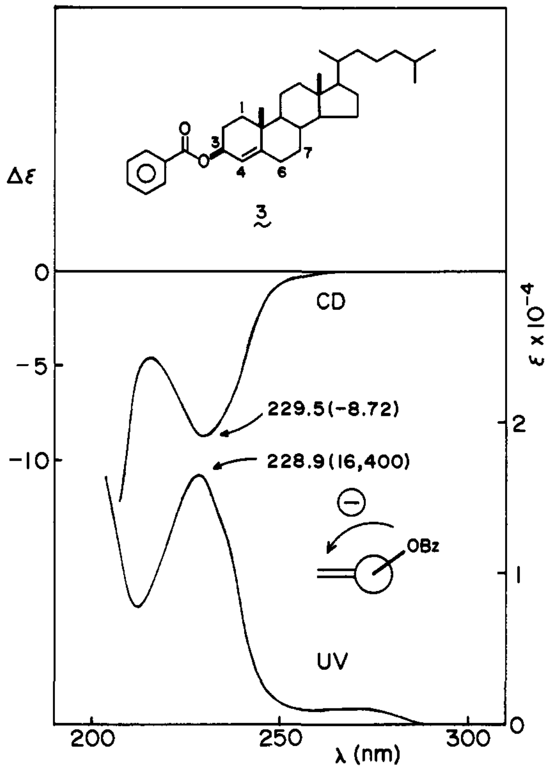

Figure 2. CD and UV spectra of chloest-4-en-3β-yl benzoate (**3**) in EtOH.

In addition to the intense $\pi \rightarrow \pi^*$ (or $\pi_x \rightarrow \pi_x^*$) transition, a C–C double-bond chromophore has additional weak $\pi \rightarrow \sigma^*$ and $\pi_x \rightarrow \pi_y^*$ transitions.[5] Moreover, since the olefinic chromophore is also asymmetrically perturbed by allylic substituents[6]

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[1] (a) Harada, N.; Nakanishi, K. *Acc. Chem. Res.* **1972**, *5*, 257. (b) Harada, N.; Uda, H. *J. Am. Chem. Soc.* **1978**, *100*, 8022. (c) Harada, N.; Tamai, Y.; Takuma, Y.; Uda, H. *Ibid.* **1980**, *102*, 501 and references cited therein. (d) Harada, N.; Nakanishi, K. "Circular Dichroic Spectroscopy—Exciton Coupling in Organic and Bioorganic Stereochemistry"; University Science Books: Mill Valley, CA, in press.

[2] Koreeda, M.; Harada, N.; Nakanishi, K. *J. Am. Chem. Soc.* **1974**, *96*, 266.

[3] Stich, K.; Rotzler, G.; Reichstein, T. *Helv. Chim. Acta* **1959**, *42*, 1480.

[4] The exciton chirality of nondegenerate systems is theoretically defined by the quadruple product, $\mathbf{R}_{ij}\cdot(\mu_{i0a} \times \mu_{j0b})V_{ij}$, where $\mathbf{R}_{ij}$ is interchromophoric distance, μ_{i0a} and μ_{j0b} are electric transition moments of chromophores *i* and *j*, respectively, and V_{ij} is interaction energy.

[5] Levin, C. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1972**, *94*, 3446.

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Table I. CD Data of Allylic Alcohol Benzoates in Ethanol

benzoate	chirality	CD λ_{ext}, nm ($\Delta\epsilon$)
5α-cholest-2-en-1α-yl (**1**)	(+)	228.2 (+12.7)
5α-cholest-1-en-3β-yl (**2**)	(+)	228.2 (+11.5)
cholest-4-en-3β-yl (**3**)	(−)	229.5 (−8.7)
cholest-4-en-3α-yl (**4**)	(+)	229.0 (+11.5)
6β-hydroxycholest-4-en-3β-yl (**5**)	(−)	229.5 (−8.9)
3β-hydroxycholest-5-en-4β-yl (**6**)	(+)	230.0 (+6.4)
3β-hydroxycholest-4-en-6β-yl (**7**)	(−)	233.0 (−4.7)
3β-acetoxy-5α-cholest-7-en-6α-yl (**8**)	(+)	231.0 (+3.0)
3β-acetoxy-5α-cholest-7-en-6β-yl (**9**)	(−)	230.6 (−11.8)
3β-hydroxycholest-5-en-7α-yl (**10**)	(−)	229.0 (−11.8)
3β-hydroxycholest-5-en-7β-yl (**11**)	(+)	229.5 (+7.3)
3β-acetoxycholest-5-en-7β-yl (**12**)	(+)	229.5 (+4.9)

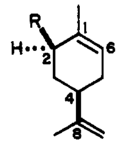
and/or skeletal strain of the double bond, overlap of additional Cotton effects complicates the CD curve of the double-bond chromophore. On the other hand, since the benzoate chromophore is strain-free, the 230-nm benzoate transition is mainly affected by the 195-nm allowed $\pi \rightarrow \pi^*$ transition of the double bond as a result of the dipole–dipole coupling mechanism in nondegenerate systems.

The CD spectra of cholest-4-en-3β-yl benzoate (**3**) is shown in Figure 2. In the region of the benzoate $\pi \rightarrow \pi^*$ transition around 229 nm, the spectrum exhibits a negative Cotton effect, the sign of which is in accordance with the negative chirality between the benzoate and double-bond chromophores. The negative CD ellipticity observed below 210 nm is in apparent disagreement with the theoretical expectation that the signs of the first and second Cotton effects should be opposite to each other.[7] This intense ellipticity is presumably due to the participation of the benzenoid ^{1}B transition (~200 nm) of the benzoate chromophore and/or the CD activity of the double-bond moiety as discussed above. Other pertinent examples are listed in Table I.

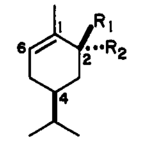
As in the case of the dibenzoate chirality method,[1] para-substituted benzoate chromophores (Me, Cl, Br, OMe, NO_2, and NMe_2) can also be used in the present method. Table II lists the examples of the *p*-nitrobenzoates of monoterpene alcohols. The fact that the sign of the exciton chirality between the benzoate and double-bond chromophore is not affected by conformational change greatly simplifies application of the present method. For instance, in the case of (*R*)-2-cyclohexen-1-yl benzoate, the cyclohexene ring can adopt two half-chair conformations (quasi-equatorial and -axial benzoates). In both conformers, the exciton chirality between the benzoate and double-bond chromophores is positive *irrespective of the cyclohexene conformation*; this is in contrast to the case of cyclohexenone systems where conformational inversions lead to reversal in enone helicity. Thus, in the present case, a positive benzoate Cotton effect leads to an *R* configuration in a straightforward manner.

All chiroptical data including the case of monocyclic compounds are in agreement with the exciton chirality between the benzoate and double-bond chromophores. The present CD exciton method for determining the absolute stereochemistry of *allylic alcohols* is based on theoretical grounds and covers the empirical Mills' rule,[8] Brewster's rule,[9] and the benzoate sector rule.[10] It is extendable to larger rings and acyclic systems where conformations of the allylic benzoates are known.

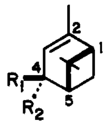
Table II. CD Data of Allylic Alcohol *p*-Nitrobenzoates in Ethanol



14, R = OBz-p-NO_2



15, R_1 = OBz-p-NO_2
R_2 = H
16, R_1 = H
R_2 = OBz-p-NO_2



17, R_1 = OBz-p-NO_2
R_2 = H
18, R_1 = H
R_2 = OBz-p-NO_2

p-nitrobenzoate	chirality	CD λ_{ext}, nm ($\Delta\epsilon$)
cholest-4-en-3β-yl (**13**)	(−)	263.0 (−3.22)
(2*R*,4*R*)-1(6),8-*p*-menthadien-2-yl (**14**)	(+)	262.0 (+5.84)
(2*S*,4*S*)-1(6)-*p*-menthen-2-yl (**15**)	(−)	261.0 (−5.64)
(2*R*,4*S*)-1(6)-*p*-menthen-2-yl (**16**)	(+)	258.0 (+7.39)
(1*S*,4*S*,5*S*)-2-pinen-4-yl (**17**)	(+)	264.4 (+5.11)[a]
(1*S*,4*R*,5*S*)-2-pinen-4-yl (**18**)	(−)	262.0 (−5.45)[a]

[a] The $\Delta\epsilon$ values are corrected on the basis of the optical purity (72.6%) of samples.

Acknowledgment. This investigation was supported in part by grants from the Ministry of Education, Japan (No. 447018), and NIH (CA-11572).

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Additivity Relation Found in the Amplitudes of Exciton-Split Circular Dichroism Curves of Pyranose Benzoates

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Received December 22, 1981

When two or more chromophores absorbing strongly around the same wavelength are closely located in space, the system gives rise to a Davydov-split[1] circular dichroism (CD) curve, the sign of which reflects the chiralities of the interacting transition moments. This splitting is due to the so-called coupled oscillator theory[2] and is the only means other than the X-ray Bijvoet method for determining the absolute configuration or conformation of molecules in a nonempirical manner.

The exciton chirality method,[3] an extension of the dibenzoate chirality method,[4] is based on this coupled oscillator theory and has been applied to a wide variety of compounds.[5] A systematic investigation of the CD of over 40 sugar benzoates, an extension

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