Table II. Comparison of the Factors Involved in the Goering–Schewene Diagrams for 2-Norbornyl Derivatives

Norbornyl	$\Delta F^{\circ}_{exo} - \Delta F^{\circ}_{endo}$, kcal mol^{-1}	$\Delta F^{\ddagger}_{exo} - \Delta F^{\ddagger}_{endo}$, kcal mol^{-1}	$\Delta\Delta F$, kcal mol^{-1}	Product ratio— Calcd	Obsd
2-Hydrogen[a]	−1.3	4.5	5.8	17,900	5000
2-Methyl[b]	−0.2	4.0	4.2	1,200	999
2-*tert*-Butyl	1.9	3.6	1.7	17.6	19

[a] Reference 9. [b] Reference 8.

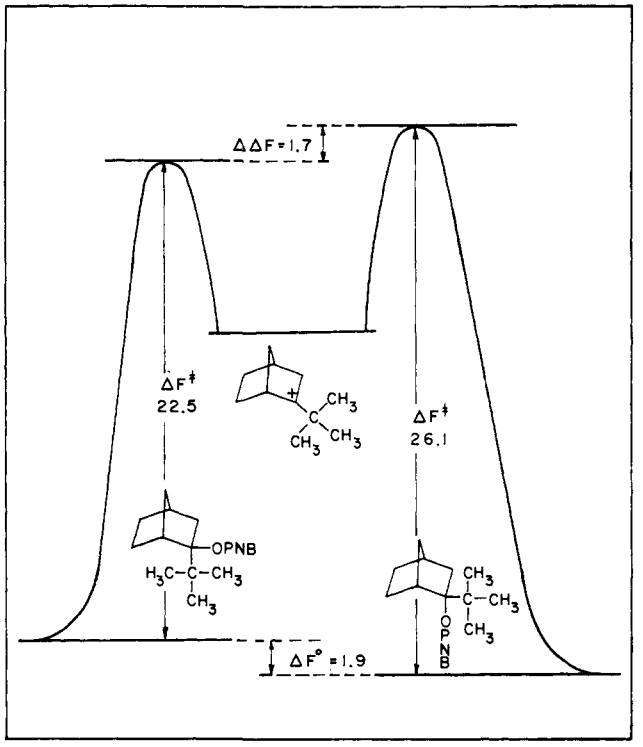

Figure 1. Free-energy diagram for the solvolysis of 2-*tert*-butyl-2-norbornyl *p*-nitrobenzoates in 80% aqueous acetone at 25°. (All values in kcal mol^{-1}.)

Schewene diagram can be constructed (Figure 1). The diagram reveals that the difference in energy between the two transition states is small, only 1.7 kcal mol^{-1}. This is consistent with the observed distribution of the cationic intermediate between exo and endo alcohols of 95:5.

We now have the data to make a highly significant comparison of the factors responsible for the major changes in the exo:endo product ratios for norbornyl, 2-methylnorbornyl, and 2-*tert*-butylnorbornyl. These are summarized in Table II.

It now becomes clear that the marked difference in the stereoselectivities exhibited by the distribution of the intermediate between exo and endo products arises not from major differences in the energies of activation for the solvolysis, such as would be anticipated for differences in σ participation, but reflect instead major differences in the ground-state energies of the exo and endo products. Consequently, it is this factor, rather than differences in σ participation, which appears to be primarily responsible for the major differences in the stereoselectivities of product formation.

A further major implication of the present results should be pointed out. It has been argued that the steric explanation for the high exo:endo rate ratio for 2-methyl-2-norbornyl[8,13] cannot be extrapolated to the high exo:endo rate ratio for norbornyl itself, in view of the large differences in the steric requirements of the 2-H and 2-Me substituents.[14] This argument for a large α-steric effect is now rendered somewhat questionable in view of the essential constancy in the exo:endo rate ratio which has now been established for the 2-H, 2-Me, and 2-*t*-Bu norbornyl derivatives, in spite of the large changes in the steric requirements of these 2 substituents.

(14) G. D. Sargent in "Carbonium Ions," Vol. III, G. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N. Y., 1972, Chapter 24.

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Exciton Chirality Method as Applied to Conjugated Enones, Esters, and Lactones

Sir:

The chiral interaction between two or more isolated but spatially close chromophores, which give rise to Davydov-split Cotton effects[1] ("exciton chirality method"[2]) is one of the most reliable optical methods for studies of absolute configurations or conformations. In this communication we have extended this method to conjugated enones, esters, and lactones. The examples shown in Table I demonstrate that a *positive chirality*, **1**, between electric transition moments of diverse carbonyl-containing chromophores **2–4** resulted in exciton-split cd curves having a *positive* first Cotton effect. Experimental curves are corroborated by nonempirical calculations as exemplified for the case of quassin **12** (Figure 2).

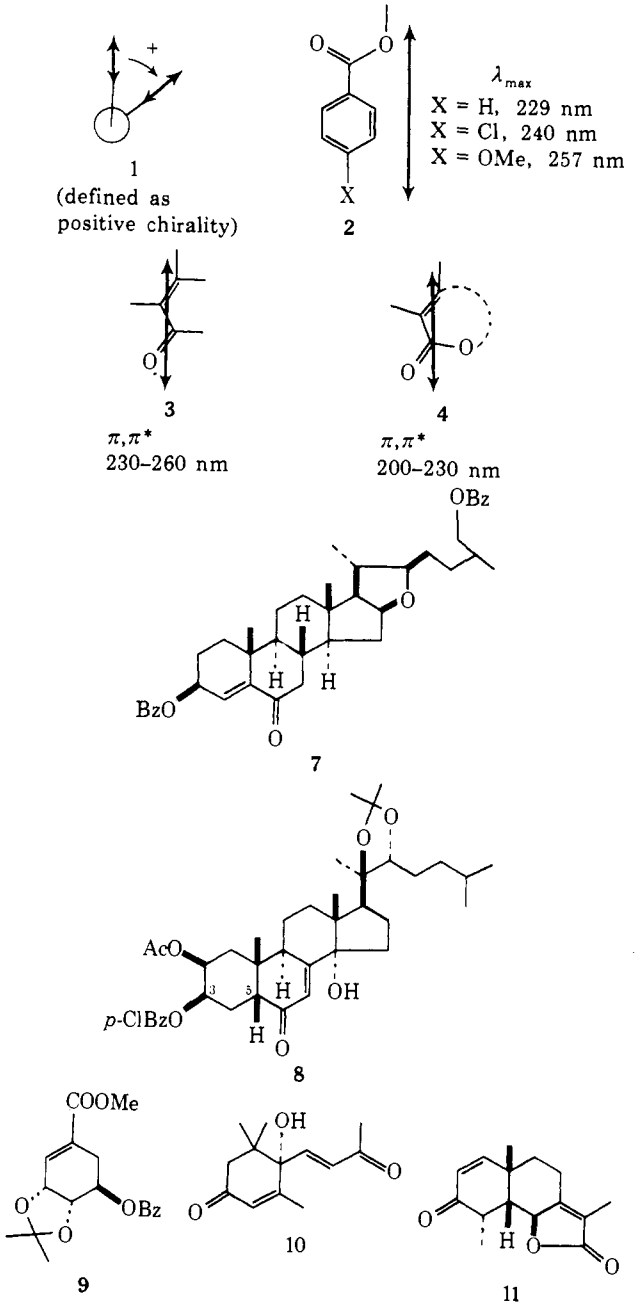
Comments on Table I are as follows. (1) The benzoate intramolecular charge transfer transitions[3] or the ^1L_a maxima[4] at 230 nm (ϵ 14,000) interact with enone π–π^* maxima at 230–260 nm (ϵ 7000–15,000) to give split cd curves which determine the enone–hydroxyl chirality (entries 1–7); whether the 205–230 nm enone cd extrema[5] are involved or not is unclear, but for practical purposes it need not be considered. (2) Note the differences between the exciton-split curve of the enone–benzoate (Figure 1, curve a) and the cd of

(1) (a) S. F. Mason, *J. Chem. Soc. B*, 370 (1966); (b) N. Harada and K. Nakanishi, *J. Amer. Chem. Soc.*, **91**, 3989 (1969).
(2) See following review: N. Harada and K. Nakanishi, *Accounts Chem. Res.*, **5**, 257 (1972).
(3) S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954).
(4) H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962.
(5) (a) L. Velluz, M. Legrand, and R. Viennet, *C. R. Acad. Sci.*, **261**, 1687 (1965); (b) K. Kuriyama, M. Moriyama, T. Iwata, and K. Tori, *Tetrahedron Lett.*, 1661 (1968); (c) A. W. Burgstahler and R. C. Barkhurst, *J. Amer. Chem. Soc.*, **92**, 7601 (1970); (d) R. N. Totty and J. Hudec, *Chem. Commun.*, 785 (1971).

Table I. Exciton Split Cd Data Involving Conjugated Enone, Lactone, and Ester Chromophores[a]

Entry	Compound	Chirality	Δε (nm) 1st	Δε (nm) 2nd	Solvent[b]
1	3β-Hydroxycholest-5-en-7-one				
a	3-Benzoate	(+)	+7.3 (237)	−18.9 (217)	M
b	3-*p*-Chlorobenzoate (**5**)	(+)	+16.7 (246)	−21.6 (221)	M
2	6β-Hydroxycholest-4-en-3-one				
a	6-Benzoate	(−)	−15.5 (241)	+21.1 (211)	M
b	6-*p*-Chlorobenzoate	(−)	−24.4 (247)	+23.0 (224)	M
c	6-*p*-Methoxybenzoate	(−)	−16.8 (259)	+21.4 (238)	M
3	6α-Hydroxycholest-4-en-3-one				
a	6-Benzoate	(+)	+13.5 (238)		M
b	6-*p*-Chlorobenzoate	(+)	+19.9 (247)		M
4	7α-Hydroxycholest-4-en-3-one 7-benzoate	(+)	+13.1 (250)	−3.3 (230)	M
5	Diosgenin derivative **7**	(−)	−25.1 (242)	+3.2 (221)	D
6	3β,14α-Dihydroxy-5α-cholest-7-en-6-one 3-*p*-Chlorobenzoate	(−)	−14.7 (250)	+8.9 (228)	M/D
7	Ponasterone A derivative **8**	(−)	−7.4 (251)	+7.7 (228)	M/D
8	Shikimic acid derivative **9**	(+)	+6.5 (228)		M
9	Dehydrovomifoliol (**10**)[c]	(+)	+38.4 (242)	−30.2 (208)	M
10	γ-Metasantonin (**11**)	(−)	−23.0 (228)	+11.3 (208)![d]	M

[a] Cd spectra were measured on Carry 60. [b] M, methanol; D, dioxane; M/D, methanol–dioxane (9–1). [c] M. Koreeda, G. Weiss, and K. Nakanishi, *J. Amer. Chem. Soc.*, **95**, 239 (1973). [d] !, last reading.



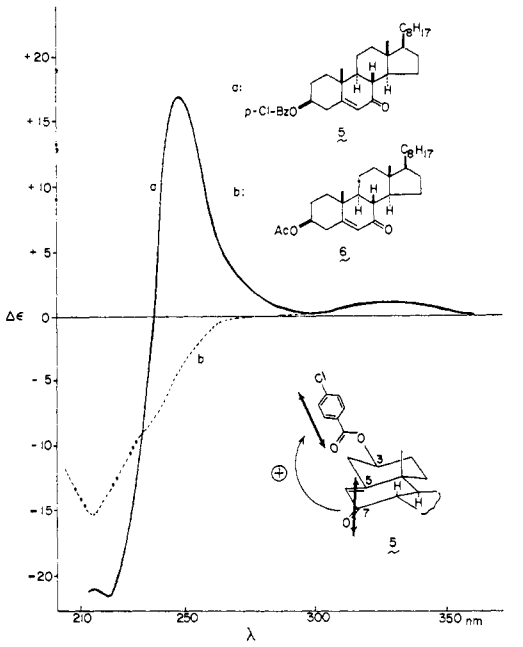


Figure 1. Circular dichroism spectra of 3β-hydroxycholest-5-en-7-one 3-*p*-chlorobenzoate (**5**) (curve a) and 3-acetate (**6**) (curve b) in methanol.

the noninteracting enone–acetate (curve b). It is advisable to choose a para-substituted benzoate having its long axis transition maximum close to the enone π–π^* maximum, because of greater magnitude of the resulting split cd maxima (see entries 2a, b, and c). (3) As seen in entries 6 and 7, the enone–benzoate interaction is present in systems other than homoallylic (entries 1 and 4) and allylic (entries 2, 3, and 5). In some cases, the second Cotton effect is very weak or virtually unobservable (entries 3, 5, and 8); the reason for this is still not clear,[1b,6] but it does not detract from the utility of the method as the wavelength of the first Cotton effect remains unchanged. (4) Entry 10 (γ-metasantonin **11**) shows that the exciton chirality method should be applicable to numerous sesquiterpenoids.

(6) G. Gottarelli, S. F. Mason, and G. Torre, *J. Chem. Soc. B*, 1349 (1970).

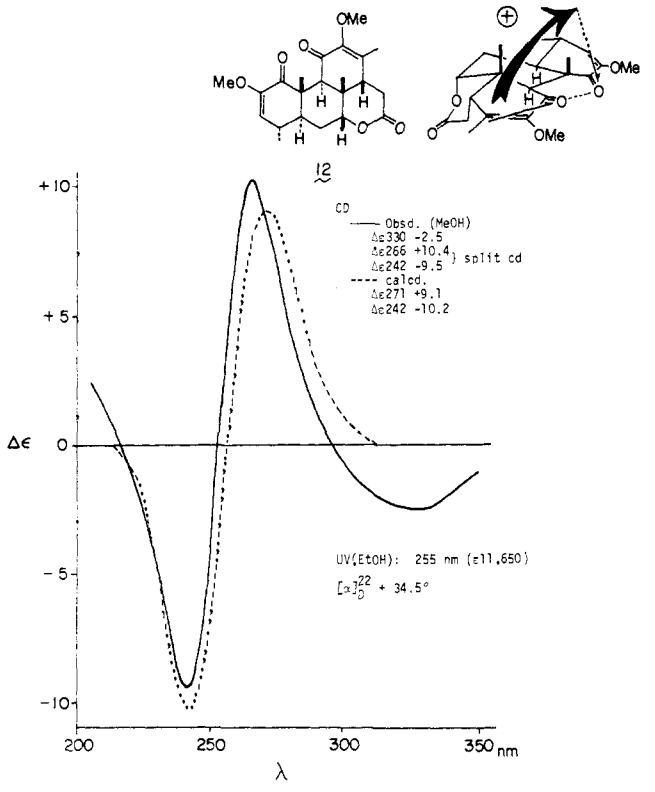


Figure 2. Circular dichroism spectra of quassin **12**: (—) observed in methanol, (-----) calculated.

The absolute configuration of plant bitter principles, the decanortriterpenoids exemplified by quassin, **12**,[7] is based on biosynthetic considerations and X-ray analysis of biogenetically related compounds.[8]

The excellent agreement seen between the observed and calculated cd curves of quassin (Figure 2) not only establishes the absolute configuration of quassin itself but also proves that the observed cd of quassin around 250 nm is due to exciton splitting.[9]

Values of transition dipole r and $1/e$-width $\Delta\sigma$ of the α-methoxy-α,β-enone were obtained from the uv of 3-methoxycholest-3-en-2-one in ethanol (r = 0.628 Å, $\Delta\sigma$ = 3043.0 cm^{-1}), and the wave number of the transition σ_{max} was approximated with that of quassin itself (σ_{max} = 39,215.6 cm^{-1}). The coordinate of each atom was determined by assuming that the B ring adopts an ideal chair conformation and the enone system is planar. The point dipole was assumed to be located at the mid point of the central single bond in the enone. The π–π^* transition dipole direction was estimated by the Pariser–Parr–Pople molecular orbital method (θ = 44.83°, Figure 3).

The examples given clearly indicate the wide applicability of the exciton chirality method to conjugated enones, esters, and lactones and obviously to numerous other chromophores. The chromophores can be present in the molecule or can be introduced by derivatization. Finally, when employing the benzoate rule[10] (based on single measurements at sodium D line) to deduce the absolute configuration of secondary hydroxyl groups, great caution should be taken to ascertain that the benzoate group is not interacting with nearby chromophores.

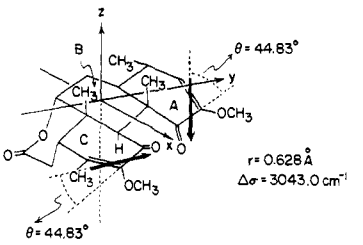


Figure 3. The positions of two transition dipoles in quassin **12**.

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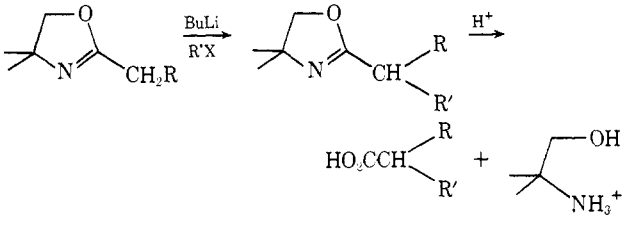
Synthesis *via* 2-Oxazolines. IV. An Asymmetric Synthesis of 2-Methylalkanoic Acids from a Chiral Oxazoline

Sir:

We wish to report an asymmetric synthesis of 2-methylalkanoic acids, **6**, which leads to either the *S*-(+) or *R*-(−) enantiomers in *optical yields of 73–84%* and, furthermore, allows recovery of the chiral reagent for recycling purposes. The method relies on our earlier observation[1] that 2-oxazolines may be elaborated to higher homologs which are hydrolyzed to α-alkylated carboxylic acids (Scheme I). If the latter scheme could

Scheme I



be implemented with a chiral heterocycle of high optical purity, the potential exists for transferring its chirality to the alkylated side chain and, hence, upon hydrolysis would provide optically active α-substituted alkanoic acids. The sequence which follows bears out this prediction.

Condensation of the readily available[2,3] (1*S*,2*S*)-(+)-1-phenyl-2-amino-1,3-propanediol (**1**) ([α]^{22}°D

(7) J. D. Connolly, K. H. Overton, and J. Polonsky, *Progr. Phytochem.*, **2**, 385 (1970).

(8) W. A. C. Brown and G. A. Sim, *Proc. Chem. Soc., London*, 293 (1964).

(9) The *negative* cd at 320 nm is due to the n–π^* transition. However, the D line rotation is *positive* because of the strongly positive extremum at 266 nm.

(10) J. H. Brewster, *Tetrahedron*, **13**, 106 (1961).

(1) A. I. Meyers and D. L. Temple, *J. Amer. Chem. Soc.*, **92**, 6644, 6646 (1970).

(2) The authors are grateful to Drs. George Moersch and Harry Crooks of Parke-Davis, Ann Arbor, Mich. for generous samples of (+)- and (−)-**1**. The (+) enantiomer is available commercially from Strem Chemicals, Inc., Danvers, Mass.

(3) The absolute configuration of (−)-**1** has been determined: J. D. Dunitz, *J. Amer. Chem. Soc.*, **74**, 995 (1952).