over anhydrous $MgSO_4$. Concentration in vacuo afforded the crude amides, **3**/**4** and **5**/**6**.

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Supplementary Material Available: Complete spectral data for all new compounds (11 pages). Ordering information is given on any current masthead page.

Synthesis and Chiroptical Properties of γ-Substituted Rigid and Conformationally Flexible Systems Having 1,3-Diene and α,β-Unsaturated Carbonyl Chromophores. The Planar Diene Rule

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Abstract: The syntheses of chiral (*aS*)-(5-hydroxyadamantylidene)- and (*aS*)-(5-methyladamantylidene)acetaldehyde and the corresponding adamantylidenepropene (rigid system) as well as (*aS*)-(4-hydroxycyclohexylidene)acetaldehyde and (*aS*)-(4-hydroxycyclohexylidene)propene (flexible system) are described. The effects of the γ-hydroxy and γ-methyl substituents on the π–π* Cotton effects of both systems are discussed as is the application of the "planar diene rule" to these systems. The adamantyl system provides a means to directly determine $\delta(\Delta\epsilon)$ for an equatorial substituent, which in turn can be used to determine the contribution that an axial substituent makes to the $\Delta\epsilon$ of a conformationally mobile system.

In recent papers from this laboratory the chiroptical properties of substituted cyclohexylidenepropenes and related trienes and α,β-unsaturated carbonyl compounds have been reported.[1] On the basis of experimental data a simple sector rule was proposed for the planar transoid diene chromophore attached to the cyclohexylidene moiety (Figure 1).

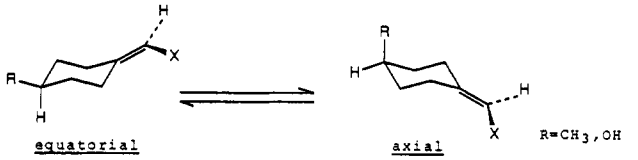
The "planar diene rule" was applied successfully to numerous methyl-substituted cyclohexylidenepropenes and structurally related α,β-unsaturated aldehydes.[1] This rule relates the sign of the long-wavelength π–π* transition in cyclohexylidene-substituted planar *s-trans*-butadienes and planar *s-trans*-acroleins with their absolute configuration.

The characteristic feature of these systems (Figure 1) is the presence of a transoid chromophore and a cyclohexane ring in a chair conformation, in which the 4-methyl (γ) substituent occupies (>95%) an equatorial position. As it is the methyl substituent which defines the chirality of the system, the following questions arise: (1) is the effect of the strong predominance of ring conformation with equatorial methyl substituent responsible for the observed rotatory power of the system (Scheme I) and (2) is the optical activity of the system influenced by the nature of the substituent in a cyclohexylidene ring?

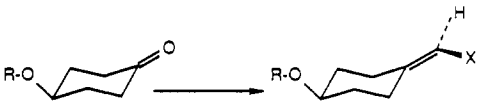
We have previously studied the conformationally flexible system substituted with a methyl group in the γ-position[1] and we have now selected, for comparison, the polar hydroxy group (R = OH) (Scheme I). Moreover, at equilibrium, the hydroxyl group has been shown to exist less in the equatorial position than the methyl group.[2] The standard free energy change, $\Delta G°_{25}$, for methylcyclohexane is 1.7 kcal/mol and for cyclohexanol it is 0.5 kcal/mol.[2,3] These values equate to approximately 95% equatorial for the methyl group and 70% for the hydroxyl group. The "flexible system" molecules that we have selected for investigation are the 4-hydroxycyclohexylidene derivatives **5**, **7**, **9**, and **11** (Scheme II).

In order to establish the nature of the effect displayed by the chirality-defining substituent (R in Figure 1), it was also necessary

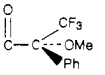
Scheme I



Scheme II



1, R = H
2, R = $SiMe_2$-*t*-Bu

no.	R	X	abs config
3	$SiMe_2$-*t*-Bu	COOH	(*aS*)-(+)
4	$SiMe_2$-*t*-Bu	COOMe	(*aS*)-(+)
5	H	COOMe	(*aS*)-(−)
6	$SiMe_2$-*t*-Bu	CHO	(*aS*)-(+)
7	H	CHO	(*aS*)-(−)
8	$SiMe_2$-*t*-Bu	$CH{=}CH_2$	(*aS*)-(−)
9	H	$CH{=}CH_2$	(*aS*)-(+)
10	$SiMe_2$-*t*-Bu	COMe	(*aS*)-(+)
11	H	COMe	(*aS*)-(−)
12		COOMe	

to obtain a conformationally rigid system with high symmetry for comparison. An interesting system which meets these criteria is the adamantane structure. This system has previously been explored by, inter alia, Djerassi,[4] Snatzke,[5] and Lightner[6] in their

† Visiting Professor from the Department of Chemistry, A. Mickiewicz University, Poznan, Poland.

(1) (a) Duraisamy, M.; Walborsky, H. M. *J. Am. Chem. Soc.* **1983**, *105*, 3264. (b) Gawronski, J. K.; Walborsky, H. M. *J. Org. Chem.* **1986**, *51*, 2863.
(2) Hirsch, J. A. *Top. Stereochem.* **1967**, *1*, 199.
(3) Bushweller, C. H.; Beach, J. A.; O'Neil, J. W.; Rao, G. V. *J. Org. Chem.* **1970**, *35*, 2086.

0002-7863/87/1509-6719$01.50/0

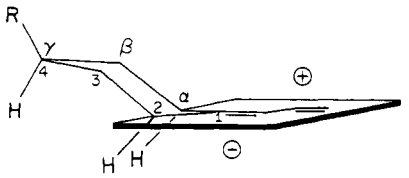


Figure 1.

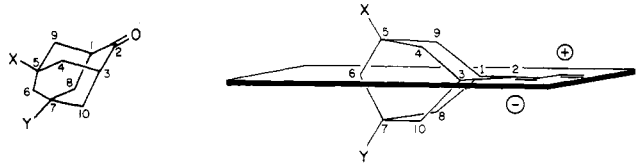


Figure 2.

octant rule studies on substituted 2-adamantanone and their effect on the CD of the n → π* transition.[4-6] Of course, a 5-substituted adamantanone is achiral and is therefore not amenable for a similar study. However, the 5-substituted 2-adamantylidenepropenes and the 5-substituted 2-adamantylideneacetaldehydes are chiral and hence the effect of the γ-substituent on the CD of π–π* transitions of the chromophore and the use of the planar diene rule can now be evaluated (Figure 2).

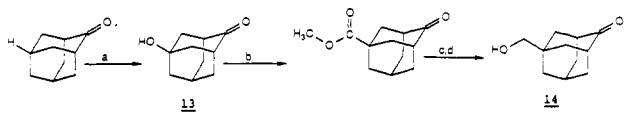
It should be noted that placing the diene (or and α,β-unsaturated aldehyde) chromophore in a plane also places carbons 1, 2, 3, and 6 in the same plane. Moreover, carbon-5 and ring CH_2-4 and -9 are located in (+)-space and carbon-7 and ring CH_2-8 and -10 are in (−)-space, thus canceling out each other's contribution. It should also be noted that when X = Y = R both enantiomeric conformations shown in Scheme I are present in the adamantane structure, connected by C-6, and the structure becomes achiral. It is only when X ≠ Y on C-5 and C-7, respectively, that we have chirality. When X equals a substituent other than hydrogen and Y = H, then we have a *direct comparison* between the effect of substituent X vs hydrogen on the π–π* Cotton effect.

Syntheses

Conformationally Flexible System. The preparation of the derivatives of (4-hydroxycyclohexylidene)acetic acid from 4-hydroxycyclohexanone (**1**) by the Wadsworth–Emmons reaction required the protection of the hydroxyl function in **1**.[7] The use of the *tert*-butyldimethylsilyl group seemed best suited since there was a need for a facile deprotection of the oxygen function at a later stage. The alcohol **1** was silylated with high yield and the product (**2**) was condensed with triethyl phosphonoacetate to give, after saponification, the desired acid **3**. It is noteworthy that no isomerization to the deconjugated acid was observed,[7] but some (6%) silylated acid **3** underwent cleavage of the silyloxy group to give the readily separable (4-hydroxycyclohexylidene)acetic acid. The resolution of the silyloxy acid **3** with (*S*)-(−)-α-methylbenzylamine turned out to be tedious but it yielded the optically active product **3** with $[\alpha]_{546}$ +2.8°, yield 21%.[8]

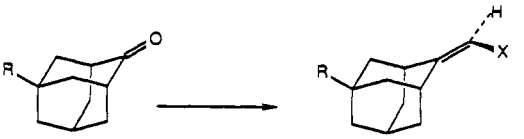
The enantiomeric excess of **3** was established by converting **5** to the Mosher ester[9] **12**. The signals of the diastereotopic CF_3 group in **12** were base line separated and the ^1H signals in the methoxy and carbomethoxy groups could also be resolved upon addition of $Eu(Fod)_3$. The partially resolved **3**, $[\alpha]_{546}$ +2.8°, was found to have 63 ± 3% ee.

Scheme III[a]



[a] (a) HNO_3; (b) $HCOOH/H_2SO_4$, MeOH; (c) $HOCH_2CH_2OH/H^+$; (d) $LiAlH_4$, H_3O^+.

Scheme IV



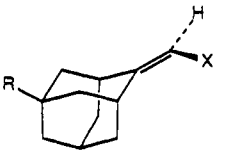
13, R = OH
14, R = CH_2OH

no.	R	X	abs config
15	OH	COOH	(*aS*)-(−)
16	OH	COOMe	(*aS*)-(−)
17	OH	CHO	(*aS*)-(+)
18	$OSiMe_2$-*t*-Bu	CHO	(*aS*)-(+)
19	OH	$CH{=}CH_2$	(*aS*)-(−)
20	$OSiMe_2$-*t*-Bu	$CH{=}CH_2$	(*aS*)-(−)
21	OH	COMe	(*aS*)-(+)
22	$HOCH_2$	COOH	(*aS*)-(−)
23	$HOCH_2$	COOMe	(*aS*)-(−)
24	Me	CH_2OH	(*aS*)-(−)
25	Me	CHO	(*aS*)-(−)
26	Me	$CH{=}CH_2$	(*aS*)-(−)
27	Me	$COCH_3$	(*aS*)-(−)
28	Me	COOMe	(*aS*)-(−)

The absolute configurations of chiral **5**, **7**, **9**, and **11** were readily established by use of the exciton chirality method[10] as applied to the benzoate derivatives of each of these compounds.[11] All compounds shown in Scheme II have the (*aS*) absolute configuration.

The synthesis of **7**, **9**, and **11** from **4** followed the well-established sequence of reactions which avoid racemization.[12] Reduction of **4** with $LiAlH_4/AlCl_3$ provided the corresponding allylic alcohol, which was oxidized with MnO_2 to yield the α,β-unsaturated aldehyde **6**. Wittig reaction (methyltriphenylphosphonium bromide and *n*-butyllithium) on the aldehyde **6** produced the diene **8**. Addition of methyllithium to **6** followed by MnO_2 oxidation gave the enone **10**. Silylated products **4**, **6**, **8**, and **10** were treated with $(n\text{-}Bu)_4NF$ to provide the desired hydroxy compounds **5**, **7**, **9**, and **11**, respectively. The deprotection of **6** and **10** was accompanied by substantial C=C bond migration into the ring, as well as other side reactions, leading to difficulty in isolating pure products. To circumvent this problem it was found necessary to first remove the silyl protecting group from the allyl alcohol obtained by $LiAlH_4/AlCl_3$ reduction of **4**. The diol obtained in this manner was selectively oxidized with MnO_2 to provide the pure α,β-unsaturated aldehyde **7**. Addition of methyllithium to **7** followed by MnO_2 oxidation produced pure **11**.

Rigid System. To the best of our knowledge chiral "axially substituted" adamantylidene derivatives have not been prepared.



For comparison with our flexible system it was necessary to prepare

(4) Briggs, W. S.; Suchy, M.; Djerassi, C. *Tetrahedron Lett.* **1968**, 1097. These authors pointed out that "the adamantanone system is ideally suited for establishing quantitatively the octant contribution of various substituents...".

(5) The first paper using the adamantane system for ORD studies is by Snatzke; see: Snatzke, G.; Marquarding, D. *Chem. Ber.* **1967**, *100*, 1710.

(6) Lightner, D. A.; Bouman, T. D.; Wijekoon, W. M. D.; Hansen, A. E. *J. Am. Chem. Soc.* **1986**, *108*, 4484 and references cited therein.

(7) If unprotected, **1** yielded the deconjungated *acid*, α-(4-hydroxycyclohexenyl)acetic acid.

(8) Partial resolution could also be achieved with MOM-protected (4-hydroxycyclohexylidene)acetic acid **16** and (−)-(*S*)-α-methylbenzylamine. However, during the reaction of acid **16** with methoxymethyl chloride some (40%) deconjugation of the acid occurred.

(9) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543.

(10) Harada, N.; Nakanishi, K. *Circular Dichroic Spectroscopy. Exciton Coupling in Organic Chemistry*; University Science Books: Mill Valley, CA, 1983.

(11) Gawronski, J. K.; Reddy, S. M.; Walborsky, H. M. *J. Am. Chem. Soc.*, accompanying paper in this issue.

(12) Duraisamy, M.; Walborsky, H. M. *J. Am. Chem. Soc.* **1983**, *105*, 3252.

two series of compounds in which R was either methyl or hydroxyl and X = COOMe, CHO, COMe, and CH=CH_2. The synthetic plan is summarized in Schemes III and IV. The key compounds for resolution and absolute configuration determination were the hydroxy acids **15** and **22**. The former is the precursor of all the 5-hydroxy-substituted 2-adamantylidene derivatives, and the latter is converted into the 5-methyl-substituted 2-adamantylidene derivatives. It was anticipated that the use of hydroxymethyl substituent in the adamantane skeleton (in **22**) rather than the methyl group would not only facilitate resolution of the highly symmetrical system but would also help in the determination of enantiomeric excess via chromatographic separation of the diastereomeric hydroxy amides.[15] Furthermore, the presence of the hydroxy groups was essential for the determination of absolute configuration by forming the benzoate derivatives and using the exciton chirality method.[10,11]

The syntheses of both acids **15** and **22** start from the known 5-hydroxy-2-adamantanone (**13**), which is readily prepared from adamantanone[13] and can readily be converted to 5-(carbomethoxy)-2-adamantanone and its ethylene ketal via published procedures.[14] $LiAlH_4$ reduction and hydrolysis afforded 5-(hydroxymethyl)-2-adamantanone (**14**).

Both of the hydroxy ketones **13** and **14** (Scheme IV) were converted to the corresponding acids **15** and **22** by the Horner–Emmons reaction and both acids were resolved by using (*S*)-(−)-α-methylbenzylamine as the resolving agent. In order to determine the enantiomeric excess (ee) of the resolved hydroxy acids, the chiral acids **15** and **22** were converted to their methyl esters and treated with (*S*)-(−)-α-methylbenzylamine to form the corresponding amides. No NMR, ^1H and ^{13}C, signal separation could be detected for the diastereomeric amides. However, it was observed that the diastereomeric amides were separable by chromatography on silica gel and this permitted us to use HPLC to determine the diastereomeric excess, which turned out to be 80% de and 90% de, respectively, for the diastereomeric amides formed from **15** and **22**.

The absolute configurations of the methyl esters obtained from the resolved acids **15** and **22** as well as compounds **17**, **19**, and **21** have been established. Each of these compounds was converted to their respective benzoate derivative and the exciton chirality method[10] applied.[11] The absolute configuration was determined to be (*aS*) in each case (Scheme IV).

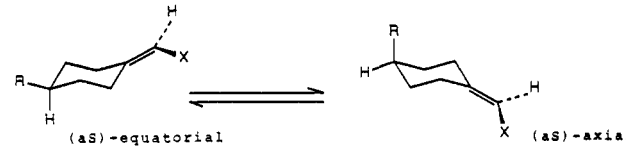
The 5-methyl group was introduced by forming the tosylate from the methyl ester of **23**. Reduction of the tosylate ester by $LiAlH_4/AlCl_3$ yielded **24**, which was then converted by previously described nonracemizing procedures[12] to the desired compounds **25–28**.

Thus, both the conformationally flexible and the rigid systems have been prepared with known optical purities and established absolute configurations.

Results and Discussion

The π–π* region Cotton effects of the 4-hydroxycyclohexylidene compounds **5**, **7**, **9**, and **11** and the 4-((*tert*-butyldimethylsilyl)-oxy)cyclohexylidene derivatives **4**, **6**, **8**, and **10** are shown in Table I. Included for comparison are also the corresponding Cotton effects of the 4-methylcyclohexylidene compounds **5m**, **7m**, **9m**, and **11m**.[1] It is seen that the Cotton effects measured at room temperature are of the same sign for each type of chromophore, i.e., negative for the 1,3-dienes and α,β-unsaturated aldehydes, which are transoidal chromophores, but positive for the α,β-unsaturated ketones and esters,[17] which are cisoidal chromophores,

Table I. CD Data for the π–π* Transition in 4-Substituted Cyclohexylidene Compounds



no.	R	X	Δε[a] (nm)
9m	Me	CH=CH_2	−3.7 (238)
9	OH		+1.6 (235)
8	$OSiMe_2$-*t*-Bu		−1.7 (239)
7m	Me	CHO	−2.1 (230)
7	OH		+0.16 (255), −1.0 (230)
6	$OSiMe_2$-*t*-Bu		−3.3 (235)
5m	Me	COOMe	+2.9 (218)
5	OH		+2.0 (221)
4	$OSiMe_2$-*t*-Bu		+1.6 (218)
11m	Me	COMe	+2.9 (235)
11	OH		+2.3 (238)
10	$OSiMe_2$-*t*-Bu		+0.9 (240)

[a] In cyclohexane.

a result consistent with our previous findings.[1] The exception is (4-hydroxycyclohexylidene)propene (**9**), which displays a positive Cotton effect at 235 nm, a result which is opposite to that predicted by the planar diene rule for the given absolute configuration.

This rather unexpected result can be nicely accounted for by the presence of a substantial amount of the axial conformer in equilibrium with the equatorial conformer. The chirality of the system composed of the ring and the diene chromophore is opposite in axial and equatorial conformers. Thus, according to the planar diene rule, the axial conformer of **9** should give a positive Cotton effect and the equatorial conformer a negative Cotton effect.

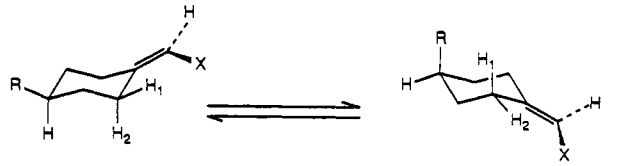
To assess the amount of the hydroxy diene conformation with the axial hydroxy group in equilibrium with the equatorial hydroxy group we have carried out MMP2 calculations on both conformers. The lowest energy conformation is the chair-like conformation with the equatorial OH group and virtually planar *s-trans*-diene chromophore. It is separated by only 0.50 kcal/mol from the second low-energy chair conformation with the axial OH group and the planar *s-trans*-diene chromophore. A chair conformation with the equatorial OH group and nonplanar *s-cis*-diene chromophore (skew angle −48.8°) lies 3.04 kcal/mol above the energy of the *s-trans*-diene conformation. Thus, it is assumed that the room-temperature equilibrium conformations of **9** consist of 70% equatorial OH and 30% axial OH (Scheme I). The net positive Cotton effect at room temperature apparently reflects the higher rotational strength of the conformer with the axial OH group. In accord with this conclusion is the observation that at −150 °C, a temperature which should reduce the axial conformer population, the CD of **9** in methylcyclohexane–isopentane showed a negative Cotton effect.[18]

With the exception of aldehyde **7** all other oxygen-substituted compounds show room-temperature Cotton effects smaller than those displayed by their methyl-substituted analogues (Table I). This, again, can be traced to the conformational effect in these systems, i.e., the presence of a substantial amount of the conformer with the axial oxygen substituent and its opposite chirality. Indeed, the two compounds for which there were no solubility problems did display significantly enhanced π–π* Cotton effects at low temperatures: **4**, $\Delta\epsilon_{-150}$ +3.5 (222 nm); **10**, $\Delta\epsilon_{-150}$ +2.7 (240 nm).

The effect of considerable admixture of the axially substituted conformer is also seen in the ^1H NMR spectra. The deshielding of the α-syn-equatorial proton H_1 in a series of 4-methyl-substituted compounds is stronger than in the 4-oxygen-substituted derivatives, even though the inductive effect of oxygen should lead to the opposite effect (Table II).

(13) Geluk, H. W. *Synthesis* **1972**, 374.
(14) LeNoble, W. J.; Srivastava, S.; Cheung, C. K. *J. Org. Chem.* **1983**, *48*, 1099.
(15) Helmchen, G.; Nill, G.; Flockerzi, D.; Schülle, W.; Youssef, M. S. K. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 62.
(16) Bal, B. S.; Childers, W. E.; Pinnick, H. W. *Tetrahedron* **1981**, *37*, 2091.
(17) The nearly planar cisoid conformation (dihedral angle 5°) of the α,β-unsaturated ester chromophore in **5** is more stable by 0.5 kcal/mol over the planar transoid conformation according to MM2 calculations. We thank Prof. A. Padwa for providing us with this datum.
(18) This observation must be viewed as tentative since the results may be affected by aggregation of the molecules and/or exciton coupling effects.[19]
(19) Sheves, M.; Kohne, B.; Friedman, N.; Mazur, Y. *J. Am. Chem. Soc.* **1984**, *106*, 5000.

Table II. Chemical Shifts (ppm) of α-Syn-Equatorial Protons



no.	R	X	H_1	H_2
9m	Me	$CH=CH_2$	2.78	*a*
9	OH		2.67	2.34
8	$OSiMe_2$-*t*-Bu		2.56	2.38
7m	Me	CHO	3.33	*a*
7	OH		3.06	2.56
6	$OSiMe_2$-*t*-Bu		2.88	2.76
5m	Me	COOMe	3.75	*a*
5	OH		3.35	2.54
4	$OSiMe_2$-*t*-Bu		3.02	2.84
11m	Me	$COCH_3$	3.69	*a*
11	OH		3.31	2.49
10	$OSiMe_2$-*t*-Bu		2.98	2.80

[a] Overlapped with other signals.

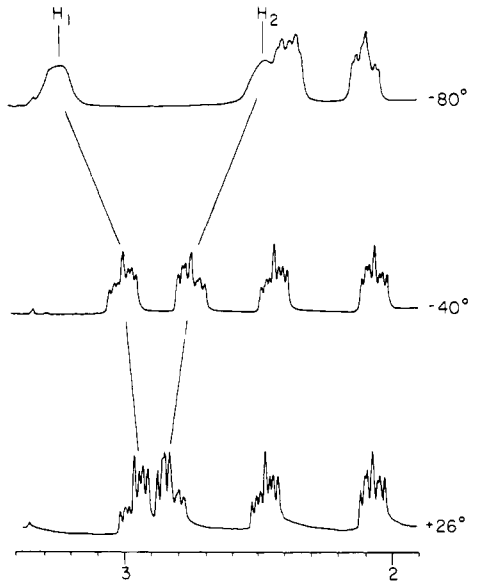


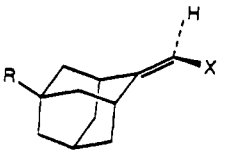
Figure 3. Allylic proton region of the 270-MHz ^1H NMR spectrum of **4** (in $CDCl_3$).

Evidently, the chemical shift of H_1 in the 4-oxygen-substituted cyclohexylidene derivative is diminished by the presence of the axial conformation, in which the proton H_1 becomes α-syn-axial and is less deshielded by the substituent X. The shielding of the α-syn-equatorial proton H_1 is also dependent on the conformation of the exocyclic π-chromophore. In the s-cisoid α,β-unsaturated esters and ketones the downfield chemical shifts are larger as compared to the s-transoid α,β-unsaturated aldehydes and 1,3-dienes, as has previously been observed for the 4-methyl-substituted cyclohexylidene derivatives.[1b]

The opposite effect is observed for the H_2 proton, as exemplified by the variable-temperature ^1H NMR spectra of **4**. With lowering temperature the signal of the H_1 proton moves downfield, whereas an upfield shift is observed for the H_2 proton. The position of signals of the remaining two allylic protons in **4** is unchanged on lowering the temperature (Figure 3).

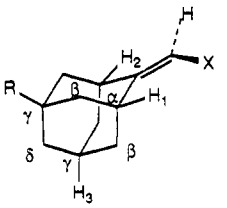
Now we report the results for the rigid 5-substituted 2-adamantylidene derivatives. The CD data are summarized in Table III. The differences between the series of 5-methyl-substituted and 5-hydroxy-substituted compounds are immediately noticeable. First, the π–π^* Cotton effects of oxygen-substituted compounds (R = OH, $OSiMe_2$-*t*-Bu) are much stronger compared to their methyl analogues (R = Me). Secondly, the sign of the π–π^* Cotton effect in the case of oxygen-substituted compounds **16–21** follows the pattern observed for the 4-methylcyclohexylidene

Table III. CD Data for the π–π^* Transition in 5-Substituted 2-Adamantylidene Compounds



no.	R	X	$\Delta\epsilon$ (nm)
26	Me	$CH=CH_2$	−0.45 (236)
19	OH		−1.4 (230)
20	$OSiMe_2$-*t*-Bu		−2.0 (230)
25	Me	CHO	−1.9 (235)
17	OH		−4.2 (231)
18	$OSiMe_2$-*t*-Bu		−5.4 (231)
28	Me	COOMe	−0.5 (227)
16	OH		+6.0 (220)
27	Me	COMe	−0.8 (240)
21	OH		+4.3 (239)

Table IV. Chemical Shifts (ppm, $CDCl_3$) of Tertiary Protons in 5-Substituted 2-Adamantylidene Compounds



no.	R	X	H_1	H_2	H_3
26	Me	$CH=CH_2$	3.05	2.41	2.02
19	OH		3.20	2.57	2.24
25	Me	CHO	3.64	2.57	2.10
17	OH		3.80	2.57	2.32
28	Me	COOMe	4.07	2.46	2.04
16	OH		4.22	2.61	2.26
27	Me	COMe	4.06	2.37	2.03
21	OH		4.21	2.53	2.25
29	H	COOEt	4.07	2.44	~2.0

derivatives of the same absolute configuration, i.e., negative for the s-trans chromophores (aldehydes **17** and **18** and dienes **19** and **20**) and positive for the s-cis chromophores (ester **16** and ketone **21**).[20] On the other hand, the π–π^* Cotton effects of the methyl-substituted compounds **25–28** are all negative, regardless of the s-trans/s-cis conformation of the conjugated chromophore.[21]

Here again, the ^1H NMR is of help in the analysis of the effect of the 5-substituent on the π–π^* Cotton effect. It can be seen from the data in Table IV that the 5-oxygenated substituent exerts a downfield shift of the remote protons in the adamantane skeleton. The tertiary protons H_1, H_2, and H_3 are broadened singlets, readily distinguishable from other signals. The allylic protons H_1 and H_2 are significantly deshielded compared to H_3.

The syn proton H_1 is shifted further downfield as compared to the anti proton H_2. In addition, the chemical shift of the syn proton H_1 is determined by the conformation of the attached α,β-unsaturated chromophore. In the case of the s-cis conformation (α,β-unsaturated ketones and esters) the downfield shift is larger (1.6 ppm) than the s-trans conformation exhibited by α,β-unsaturated aldehydes (1.0 ppm) and 1,3-dienes (0.6 ppm). Comparison of the chemical shifts of the H_1, H_2, and H_3 signals for each pair of 5-hydroxy- and 5-methyl-substituted compounds leads to the conclusion that the hydroxy group brings about an additional downfield shift of 0.15–0.16 ppm for the H_1 and H_2

(20) The planarity as well as the s-cis/s-trans conformation of the chromophores attached to the adamantylidene ring requires no further documentation in view of the evidence presented for analogous cyclohexylidene derivatives. See also: Reddy, S. M.; Goedken, V. L.; Walborsky, H. M. *J. Am. Chem. Soc.* **1986**, *108*, 2691.

(21) It should be emphasized the "planar diene rule" applies only to those molecules whose chromophore is in the s-trans conformation and planar.

Table V. Contribution of Axial and Equatorial Substituents to CD[25]

R	X	f_a	$\Delta\epsilon_{R_{ae}}$	$\Delta\epsilon_{R_e}$	$\Delta\epsilon_{R_a}$
OH	$CH{=}CH_2$	0.30	+1.6	−1.4	+8.6
$OSiMe_2$-*t*-Bu		0.25	−1.7	−2.0	−0.8
Me	CHO	0.05	−2.1	−1.9	−0.6
OH		0.30	−1.0	−4.2	+6.5
$OSiMe_2$-*t*-Bu		0.25	−3.3	−5.4	+3.0
OH	COOMe	0.30	+2.0	+6.0	−7.0
OH	COMe	0.30	+2.3	+4.3	−2.3

signals and 0.22 ppm for the H_3 signal. The difference between the effect of a 5-methyl group and a 5-hydrogen substituent is negligible as can be seen by comparing **28** and **29**.

It thus appears that the deshielding effect of the 5-hydroxy group on the H_1, H_2, and H_3 resonances is carried efficiently through a W-bond sequence, i.e., $HO{-}C_\gamma{-}C_\beta{-}C_\alpha{-}H_1(H_2)$ and $HO{-}C_\gamma{-}C_\delta{-}C_\gamma{-}H_3$. Therefore, although the hydroxy substituent is removed from the chiral chromophore, this polar substituent can make itself felt via a through σ-bond W effect[22].

In summary, the π–π^* Cotton effects are strongly influenced by the conformer population and this points to the importance of the spatial orientation of the cyclohexane C–C bonds relative to the planar conjugated chromophore (planar diene rule). Moreover, the Cotton effect is also affected by a polar substituent which can transmit its effect through σ-bonds via a W pathway.

As we have previously discussed in our evaluation of the adamantyl system, shown in Figure 2, when X equals a substituent (R) and Y = H, we have a built in reference which provides a direct comparison between the effect of R vs H on the π–π^* Cotton effect. Therefore, when R = OH and Y = H the Cotton effect observed is due to $\Delta\epsilon_{OH} - \Delta\epsilon_H$, which is $\delta(\Delta\epsilon)$,[22] a value which is characteristic of a substituent which can couple with a chromophore ($\delta\Delta\epsilon = \Delta\epsilon_R - \Delta\epsilon_H$) and is related to the reduced rotational strength of the substituent ($\delta[R] = C\delta\Delta\epsilon$).[22,23] The $\delta(\Delta\epsilon)$ values have been used to determine the contribution of alkyl groups to the $\Delta\epsilon$ values ($n \rightarrow \pi^*$) of cyclohexanone and decalone analogues.[23f] In our system we will obtain $\delta\Delta\epsilon$ *directly* as long as we keep Y = H as our internal standard. However, the $\delta\Delta\epsilon$ values obtained in this manner are limited to the substituent being in the *equatorial position* so that $\delta(\Delta\epsilon)_e = \Delta\epsilon_{R_e} - \Delta\epsilon_{H_e}$.

The $\delta(\Delta\epsilon)_e$ values can be used to determine the contribution that an axial and equatorial conformer makes to the overall $\Delta\epsilon_{R_{ae}}$ of an equilibrium mixture of conformers, such as depicted in Scheme I.

Since $\Delta\epsilon_{R_{ae}} = \Delta\epsilon_{R_a}f_a + \Delta\epsilon_{R_e}(1 - f_a)$, $\Delta\epsilon_{R_a} = (\Delta\epsilon_{R_{ae}} - \Delta\epsilon_{R_e}(1 - f_a))/f_a$.

Now $\Delta\epsilon_{R_{ae}}$ is an experimentally determined value, f_a (fraction of axial conformer at equilibrium) can be obtained from MMP2 calculations,[24] and $\Delta\epsilon_{R_e}$ can be approximated from $\delta(\Delta\epsilon)_e - \Delta\epsilon_{H_e} = \Delta\epsilon_{R_e}$ or $\delta(\Delta\epsilon)_e \approx \Delta\epsilon_{R_e}$. This approximation is made because, at this time, we do not have a value for $\Delta\epsilon_{H_e}$. However, one would expect this value to be quite small and therefore to have little effect on the overall value of $\Delta\epsilon_{R_a}$, especially if $\Delta\epsilon_{R_a}$ is large, >1.0. Table V lists the contributions that substituents make to the Cotton effect at equilibrium when in the axial and equatorial positions. The difference between contributions of axial and equatorial substituents is positive for transoid chromophores (diene and α,β-unsaturated aldehyde) and negative for cisoid chromophores (α,β-unsaturated ester and ketone).

Experimental Section[26]

4-((*tert*-Butyldimethylsilyl)oxy)cyclohexanone (2). A solution of 23.8 g (0.208 mol) of 4-hydroxycyclohexanone (**1**), 34.5 g (0.23 mol) of *tert*-butyldimethylchlorosilane, and 20.9 g (0.307 mol) of imidazole in dichloromethane (150 mL) was stirred at room temperature for 1 h. The mixture was diluted with hexane, and the solution was decanted from the crystalline deposit and filtered through silica gel. The solvents were removed in vacuo to leave a colorless liquid product **2**, yield 46.7 g (98%), sufficiently pure for further steps. The analytical sample was purified by distillation at 85 °C/1 mmHg: IR (film) 2930, 2840, 1720, 1260, 1110, 1050 cm^{-1}; ^1H NMR δ 0.10 (s, 6 H), 0.92 (s, 9 H), 1.85–2.05 (m, 4 H), 2.24 (dt, J = 15, 4 Hz, 2 H), 2.58–2.78 (m, 2 H), 4.14 (m, 1 H); MS m/e 171 ($M^+ - t$-Bu).

(*aS*)-(4-((*tert*-Butyldimethylsilyl)oxy)cyclohexylidene)acetic Acid (3). A solution of sodium triethyl phosphonoacetate (prepared at 0 °C with 39.2 mL (0.19 mol) of triethyl phosphonoacetate and 8.4 g (0.175 mol) of 50% sodium hydride in 175 mL of dimethoxyethane) was added to a solution of 40 g (0.175 mol) of ketone **2** in 100 mL of dimethoxyethane. After 1 h at room temperature the solution was partitioned between hexane and water. The hexane extract was washed with water, dried over $MgSO_4$, and evaporated. Crude ethyl (4-((*tert*-butyldimethylsilyl)-oxy)cyclohexylidene)acetate (51.2 g, 98% yield) was saponified by refluxing 1 h with 150 mL of 2 N NaOH and 150 mL of methanol. The solution was diluted with brine and extracted with ether. The water solution was carefully neutralized with 2 N HCl to give (4-hydroxycyclohexylidene)acetic acid (1.6 g, 6% yield). The methanol–ether solution was evaporated and the residue extracted with brine and ether–hexane. The water layer was acidified with 2 N HCl (160 mL) while stirred in an ice bath with diethyl ether. The ethereal layer was washed with brine, dried over $MgSO_4$, and evaporated to give **3**, 41.5 g (90% yield), mp 110–115 °C. Crystallization from hexane yielded an analytical sample: mp 118–121 °C; IR (Nujol) 3500–2400 (broad), 1680, 1635, 1275, 1260, 1210 cm^{-1}; ^1H NMR δ 0.08 (s, 6 H), 0.91 (s, 9 H), 1.60–1.80 (m, 4 H), 2.05–2.20 (m, 1 H), 2.45–2.60 (m, 1 H), 2.80–3.10 (m, 2 H), 3.96 (m, 1 H), 5.66 (s, 1 H). Anal. Calcd for $C_{14}H_{26}O_3Si$: C, 62.18; H, 9.69. Found: C, 62.21; H, 9.72.

Racemic **3** (37 g, 0.144 mol) and (*S*)-(−)-α-methylbenzylamine (18.6 mL, 0.144 mol) were dissolved in hot acetonitrile (400 mL), and the salts were left to crystallize. The salt (mp 116–130 °C) was crystallized repeatedly from acetonitrile and ethyl acetate. After 10 crystallizations the salt had mp 147–149 °C; yield 12 g. The resolved acid **3** was recovered in the standard way: yield 7.9 g (21% from the racemic acid): mp 78–81 °C; $[\alpha]^{25}_{546}$ +2.8° (*c* 1.2, cyclohexane); UV ϵ 15 700 (222.5 nm); CD $\Delta\epsilon$ −0.25 (253 nm), +1.4 (225 nm).

Methyl (*aS*)-(4-((*tert*-Butyldimethylsilyl)oxy)cyclohexylidene)acetate (4). A sample of resolved **3** was methylated with ethereal diazomethane and purified by radial chromatography (hexane–3% diethyl ether): $[\alpha]^{25}_{546}$ +2.55° (*c* 1.2, cyclohexane); IR (film) 2930, 2840, 1720, 1650, 1260, 1170, 1105, 1050, 870, 840, 780 cm^{-1}; NMR δ 0.06 (s, 6 H), 0.90 (s, 9 H), 1.55–1.80 (m, 4 H), 2.0–2.15 (m, 1 H), 2.40–2.55 (m, 1 H), 2.75–2.90 (m, 1 H), 2.90–3.05 (m, 1 H), 3.65 (s, 3 H), 3.93 (m, 1 H), 5.60 (s, 1 H); UV ϵ 17 300 (218 nm); CD $\Delta\epsilon$ −0.26 (250 nm), +1.6 (218 nm). Anal. Calcd for $C_{15}H_{28}O_3Si$: C, 63.33; H, 9.92. Found: C, 63.17; H, 9.92.

Methyl (*aS*)-(4-Hydroxycyclohexylidene)acetate (5). A sample of **4** was stirred 6 h with 1.5 equiv of 0.5 M Bu_4NF in THF. The solution was extracted with ether and the product was purified by radial chromatography (hexane–diethyl ether, 4:1): yield 50%; $[\alpha]^{25}_{546}$ −5.0° (*c* 1, cyclohexane–CH_2Cl_2); IR (film) 3380, 2990, 2940, 2860, 1720, 1660, 1440, 1180 cm^{-1}; ^1H NMR δ 1.45–1.70 (m, 2 H), 1.70 (s, 1 H), 1.85–2.05 (m, 2 H), 2.10–2.30 (m, 1 H), 2.35–2.60 (m, 2 H), 3.25–3.45 (m, 1 H), 3.70 (s, 3 H), 3.85–4.0 (m, 1 H), 5.67 (s, 1 H); UV ϵ 14 200 (217 nm); CD $\Delta\epsilon$ −0.25 (251 nm), +2.0 (221 nm). Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.61; H, 8.32.

Methyl (*aS*)-(4-(α-Methoxy-α-(trifluoromethyl)phenylacetoxy)-cyclohexylidene)acetate (12). Alcohol **5** (56 mg, 0.33 mmol) in CH_2Cl_2 (1 mL) was stirred overnight with 4-(dimethylamino)pyridine (100 mg, 0.8 mmol) and the Mosher reagent, prepared from 0.5 mmol of (+)-α-methoxy-α-(trifluoromethyl)phenylacetic acid according to the published procedure.[9] The crude product, obtained upon removal of the solvent, was analyzed by 142-MHz ^{19}F NMR in benzene-d_6 with CF_3COOH as reference. The CF_3 resonance signals of the Mosher ester were clearly

(22) Hughes, M. T.; Hudec, J. *Chem. Commun.* **1971**, 805. Powell, G. P.; Hudec, J. *Chem. Commun.* **1971**, 806.

(23) For a discussion of rotatory strength and its application; see: (a) Moscowitz, A. *Tetrahedron* **1961**, *13*, 48. Moscowitz, A. In *Optical Rotatory Dispersion*; Djerassi, C., Ed.; McGraw-Hill: New York, 1960. (b) Charney, E. *Molecular Basis of Optical Activity*; Wiley: New York, 1979. (c) Gawronski, J. K. *Tetrahedron* **1982**, *38*, 3. (d) Rosenfield, J. S.; Charney, E. *J. Am. Chem. Soc.* **1977**, *99*, 3209. (e) Lee, S.-F.; Edgar, M.; Pak, C. S.; Barth, G.; Djerassi, C. *J. Am. Chem. Soc.* **1980**, *102*, 4784. (f) Kirk, D. N.; Klyne, W. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1076. (g) Snatzke, G.; Klein, H. *Tetrahedron* **1969**, *25*, 5601.

(24) This value can be approximated reasonably well from the conformational free energy difference $-\Delta G°$ for a substituent X. Values of $-\Delta G°$ are available for a large number of substituents in the cyclohexane system.[2] These values should also apply to the 4-X-cyclohexylidenes. As a check we carried out an MMP2 calculation for X = OH, and the value obtained, $-\Delta G°_{25}$ = 0.5 kcal/mol, was almost identical with the value, 0.52 kcal/mol, that is reported for cyclohexanol in aprotic solvents.[2]

(25) It should be noted that $\Delta\epsilon_{R_{ae}}$ and $\Delta\epsilon_{R_e}$ must have values ≥1.0.

(26) See ref 1b for general experimental procedures.

split by 23 Hz, to give area ratio 163:37, which corresponds to 63 ± 3% ee of the resolved acid **3**: ^{1}H NMR δ 1.80–2.10 (m, 4 H), 2.10–2.50 (m, 2 H), 2.85–3.05 (m, 2 H), 3.58 (s, 3 H), 3.70 (s, 3 H), 5.31 (m, 1 H), 5.68 (s, 1 H), 7.35–7.75 (m, 5 H). The OMe signals at δ 3.58 and 3.70 are resolved upon addition of tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium.

(*aS*)-(4-((*tert*-Butyldimethylsilyl)oxy)cyclohexylidene)ethanol. Ester **4** (10 mmol) was reduced with $LiAlH_4$–$AlCl_3$ following the standard procedure[1] to give the product in 94% yield. This product was used in further steps without purification: IR (film) 3310, 2940, 2860, 1675, 1265, 1110, 845 cm^{-1}; ^{1}H NMR δ 0.05 (s, 6 H), 0.90 (s, 9 H), 1.45–1.60 (m, 2 H), 1.60–1.80 (m, 2 H), 1.95–2.15 (m, 2 H), 2.30–2.55 (m, 2 H), 3.80–3.90 (m, 1 H), 4.13 (d, J = 7 Hz, 2 H), 5.40 (t, J = 7 Hz, 1 H).

(*aS*)-(4-Hydroxycyclohexylidene)ethanol. The above allylic alcohol (2.30 g (9 mmol) was stirred overnight with 20 mL of 0.5 M Bu_4NF in THF. The mixture was diluted with CH_2Cl_2 and filtered through silica gel. After removal of the solvent the product was dissolved in CH_2Cl_2 and filtered, and solvent was removed to yield an oily product (1.30 g), which was used in the subsequent steps without further purification: ^{1}H NMR δ 1.30–1.70 (m, 2 H), 1.56 (br s, 2 H), 1.85–2.20 (m, 4 H), 2.25–2.40 (m, 1 H), 2.50–2.60 (m, 1 H), 3.80–3.90 (m, 1 H), 4.15 (d, J = 7 Hz, 2 H), 5.42 (t, J = 7 Hz, 1 H).

(*aS*)-(4-((*tert*-Butyldimethylsilyl)oxy)cyclohexylidene)acetaldehyde (6). The allylic alcohol (1.7 g) was oxidized with MnO_2 (10.5 g) in hexane (110 mL) at 0 °C for 2.5 h. The solution was filtered, concentrated, and filtered through a pad of $MgSO_4$. Removal of solvents gave a solid product, 1.48 g (88%). An analytical sample was purified by radial chromatography (hexane–10% diethyl ether): mp 34–36 °C; $[\alpha]^{25}_{546}$ +4.9° (*c* 1, cyclohexane); IR (film) 2940, 2860, 1685, 1640, 1265, 1120, 1055, 845, 785 cm^{-1}; ^{1}H NMR δ 0.09 (s, 6 H), 0.92 (s, 9 H), 1.75–1.85 (m, 4 H), 2.15–2.25 (m, 1 H), 2.55–2.70 (m, 1 H), 2.70–2.80 (m, 1 H), 2.80–2.95 (m, 1 H), 4.00–4.10 (m, 1 H), 5.85 (d, J = 8 Hz, 1 H), 10.01 (d, J = 8 Hz, 1 H); UV ε 50 (346 nm), 19 800 (233 nm); CD Δε +0.57 (347 nm), −3.3 (235 nm). Anal. Calcd for $C_{14}H_{26}O_2Si$: C, 66.08; H, 10.30. Found: C, 66.19; H, 10.31.

(*aS*)-(4-Hydroxycyclohexylidene)acetaldehyde (7). The diol (9 mmol) was stirred in an ice bath with MnO_2 (10 g) in a 3:1 mixture of CH_2Cl_2–$CHCl_3$ (120 mL) for 6 h. The mixture was filtered under reduced pressure and the solvents were evaporated to give 1.28 g of an oily product **7**, which was purified by radial chromatography (hexane–diethyl ether, 1:1) to yield 1.01 g (80%): $[\alpha]^{25}_{546}$ −4.0° (*c* 2, CH_2Cl_2); IR (film) 3380, 3020, 2940, 2860, 1675, 1075, 960, 865 cm^{-1}; ^{1}H NMR δ 1.60–1.80 (m, 2 H), 1.87 (br s, 1 H), 1.90–2.10 (m, 2 H), 2.15–2.35 (m, 1 H), 2.45–2.65 (m, 2 H), 3.00–3.15 (m, 1 H), 3.95–4.10 (m, 1 H), 5.88 (d, J = 8 Hz, 1 H), 10.00 (d, J = 8 Hz, 1 H); UV ε 53 (346 nm) 19 500 (232 nm); CD Δε +0.29 (346 nm), +0.16 (255 nm), −1.0 (230 nm). Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.51; H, 8.76.

(*aS*)-(4-((*tert*-Butyldimethylsilyl)oxy)cyclohexylidene)propene (8). Aldehyde **6** (0.51 g, 2 mmol) in 5 mL of dry diethyl ether was added at CCl_4–dry ice bath temperature to the ylid solution prepared from 1.43 g (4 mmol) of vacuum-dried methyltriphenylphosphonium bromide in diethyl ether (25 mL) and 1.6 mL of 2.5 M *n*-butyllithium. The mixture was allowed to warm to room temperature and after 1.5 h it was quenched with wet diethyl ether. The ethereal solution was filtered and evaporated, and the residue was filtered through silica gel using hexane as solvent. After evaporation of solvents **8** was obtained as an oil (0.343 g, 68%). The analytical sample was purified by radial chromatography with hexane as solvent: $[\alpha]^{25}_{546}$ −8.3° (*c* 1, cyclohexane); IR (film) 3075, 3035, 2940, 2860, 1655, 1605, 1265, 1110, 1055, 905, 870, 840, 780 cm^{-1}; ^{1}H NMR δ 0.07 (s, 6 H), 0.90 (s, 9 H), 1.45–1.60 (m, 2 H), 1.65–1.80 (m, 2 H), 2.00–2.20 (m, 2 H), 2.30–2.45 (m, 1 H), 2.50–2.65 (m, 1 H), 3.80–3.95 (m, 1 H), 4.97 (dd, J = 11, 2 Hz, 1 H), 5.11 (dd, J = 16.5, 2 Hz, 1 H), 5.82 (d, J = 11 Hz, 1 H), 6.59 (dt, J = 16.5, 11, 11 Hz, 1 H); UV ε 26 300 (238 nm); CD Δε −1.7 (239 nm), +1.3 (214 nm).

(*aS*)-(4-Hydroxycyclohexylidene)propene (9). Diene **8** (1 mmol) was stirred under nitrogen at room temperature with 3 mL of 0.5 M Bu_4NF in THF for 6 h. The THF was removed in vacuo, and the residue was dissolved in CH_2Cl_2 and filtered through silica gel. The product **9** was further purified by radial chromatography (hexane–diethyl ether 4:1): yield 125 mg (90%); $[\alpha]^{25}_{546}$ +8.4° (*c* 1, cyclohexane); IR (film) 3320, 3075, 3035, 2930, 2860, 1655, 1605, 1075, 1000, 975, 905 cm^{-1}; ^{1}H NMR δ 1.30–1.55 (m, 2 H), 1.52 (s, 1 H), 1.85–2.05 (m, 2 H), 2.05–2.20 (m, 2 H), 2.25–2.40 (m, 1 H), 2.60–2.75 (m, 1 H), 3.80–3.90 (m, 1 H), 5.00 (dd, J = 11, 2 Hz, 1 H), 5.12 (dd, J = 16.5, 2 Hz, 1 H), 5.84 (d, J = 11 Hz, 1 H), 6.59 (dt, J = 16.5, 11, 11 Hz, 1 H); UV ε 27 700 (237 nm); CD Δε +1.6 (235 nm); MS calcd for C_9H_{14}, 138.1045; found, 138.1046.

(*aS*)-(4-((*tert*-Butyldimethylsilyl)oxy)cyclohexylidene)acetone (10). Aldehyde **6** (0.51 g, 2 mmol) in 5 mL of dry diethyl ether was treated at 0 °C with 3 mL of 1.6 M methyllithium. After 1 h at 0 °C the solution was quenched with water and extracted with diethyl ether. The extracts were washed with water, dried over $MgSO_4$, and oxidized overnight with MnO_2 (3.5 g) at room temperature. The mixture was filtered through $MgSO_4$, and the solvent was evaporated to give **10** as a colorless oil, yield 0.49 g. This was further purified by radial chromatography (hexane–10% diethyl ether): yield 0.446 g (83%); $[\alpha]^{25}_{546}$ +3.3° (*c* 1.5, cyclohexane); IR (film) 2940, 2860, 1695, 1630, 1365, 1265, 1185, 1110, 1055, 845, 780 cm^{-1}; ^{1}H NMR δ 0.06 (s, 6 H), 0.89 (s, 9 H), 1.55–1.85 (m, 4 H), 2.00–2.15 (m, 1 H), 2.16 (s, 3 H), 2.40–2.55 (m, 1 H), 2.75–2.85 (m, 1 H), 2.90–3.05 (m, 1 H), 3.90–4.00 (m, 1 H), 6.01 (s, 1 H); UV ε 56 (330 nm), 14 400 (236 nm); CD Δε −0.07 (345 nm), +0.9 (240 nm). Anal. Calcd for $C_{15}H_{28}O_2Si$: C, 67.11; H, 10.51. Found: C, 67.15; H, 10.54.

(*aS*)-(4-Hydroxycyclohexylidene)acetone (11). Aldehyde **7** (0.28 g, 2 mmol) in THF (5 mL) was added to 10 mL of 1.6 M MeLi under N_2 at −78 °C. The mixture was allowed to warm to 0 °C and quenched with water (1 mL), and the solution was dried over $MgSO_4$ and evaporated. The residue (0.31 g) was dissolved in CH_2Cl_2 (30 mL) and stirred overnight with MnO_2 (3.5 g). The mixture was filtered, the filtrate was evaporated, and the product **11** was purified by radial chromatography (3:1 hexane–diethyl ether): yield 95 mg (31%); $[\alpha]^{25}_{546}$ −17.8° (*c* 1.5, CH_2Cl_2); IR (film) 3390, 3000, 2940, 2860, 1690, 1625, 1370, 1265, 1190, 1080, 960 cm^{-1}; ^{1}H NMR δ 1.45–1.65 (m, 2 H), 1.64 (s, 1 H), 1.90–2.10 (m, 2 H), 2.10–2.25 (m, 1 H), 2.20 (s, 3 H), 2.35–2.55 (m, 2 H), 3.25–3.40 (m, 1 H), 3.90–4.00 (m, 1 H), 6.05 (s, 1 H). UV: ε 68 sh (335 nm), 14 200 (235 nm); CD Δε −0.046 (337 nm), +2.3 (238 nm). Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.08; H, 9.17.

5-(Hydroxymethyl)-2-adamantanone (14). 5-(Carbomethoxy)-2-adamantanone ethylene ketal[14] (34 g, 0.135 mol) in dry diethyl ether (100 mL) was added at 0 °C to a solution of $LiAlH_4$ (9.5 g, 0.25 mol) in dry diethyl ether (200 mL). The mixture was allowed to stir overnight at room temperature and then excess $LiAlH_4$ was destroyed by careful addition of 2 N NaOH. The salts were filtered off and washed with ether, and solvent was removed in vacuo to give 5-(hydroxymethyl)-2-adamantanone ethylene ketal as a colorless oil: yield 29.6 g (98%); ^{1}H NMR δ 1.3–2.1 (m, 14 H), 3.23 (d, J = 6 Hz, 2 H), 3.96 (s, 4 H).

The ketal (29.5 g) in THF (250 mL) was stirred overnight with 500 mL of 1 N H_2SO_4. The solution was saturated with NaCl and neutralized with 30% NaOH solution. Extraction with diethyl ether gave 5-(hydroxymethyl)-2-adamantanone (**14**): yield 22.5 g (95%); IR (film) 3390, 2910, 2840, 1715, 1050 cm^{-1}. ^{1}H NMR: δ 1.69 (br s, 1 H), 1.7–1.9 (m, 6 H), 2.01 (br s, 4 H), 2.18 (br s, 1 H), 2.58 (br s, 2 H), 3.33 (br s, 2 H).

Methyl (*aS*)-(5-Hydroxy-2-adamantylidene)acetate (16). A suspension of 7.2 g (150 mmol) of 50% sodium hydride (washed with pentane) in dry dimethoxyethane (150 mL) was treated in an ice bath with triethyl phosphonoacetate (14.9 mL, 75 mmol). After 1 h solid 5-hydroxy-2-adamantanone (**13**) (12 g, 72 mmol) was added and the mixture was stirred overnight at room temperature. The reaction mixture was carefully decomposed with water and extracted with ether. After removal of solvents the oily residue was refluxed 1 h with a mixture of 2 N NaOH (75 mL) and methanol (25 mL). The solution was extracted twice with ether and added dropwise to a mixture of concentrated H_2SO_4 (10 mL), ice, and water. The solid product was collected and washed with water; yield of the racemic acid (**15**) was 11.4 g (75%), mp 195–198 °C. The analytical sample was obtained by recrystallization from acetone; mp 199–201 °C. The acid **15** was resolved by crystallization of its salt with (*S*)-(−)-α-methylbenzylamine from ethanol. After three crystallizations the salt had mp 213–217 °C (dec). The free acid **15** was liberated from the salt in the usual way: overall yield 20%; mp 187–189 °C; UV ε 14 000 (217.5 nm); CD Δε −0.75 (253 nm), +2.5 (222 nm). Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.23; H, 7.69. Found: C 69.12; H, 7.69.

Methyl ester **16** was prepared with the aid of ethereal diazomethane; mp 77–80 °C; $[\alpha]^{24}_{546}$ −4.48° (*c* 1, $CHCl_3$); IR (film) 3370, 2980 (w), 2920, 2840, 1700, 1645, 1480–860 cm^{-1}; ^{1}H NMR δ 1.61 (br s, 1 H), 1.65–2.05 (m, 10 H), 2.26 (br s, 1 H), 2.61 (br s, 1 H), 3.70 (s, 3 H), 4.22 (br s, 1 H), 5.61 (s, 1 H); UV ε 17 500 (220 nm); CD Δε −1.0 (252 nm), +6.0 (220 nm).

Amides of (5-Hydroxy-2-adamantylidene)acetic Acid with (*S*)-(−)-α-Methylbenzylamine. A sample of methyl ester **16**, prepared from racemic acid **15**, was heated with an excess of (*S*)-(−)-α-methylbenzylamine at 170 °C overnight. The formation of diastereomeric amides was complete according to TLC. The solution was diluted with hexane, and the semisolid products were digested with hexane–diethyl ether to remove excess (*S*)-(−)-α-methylbenzylamine. The solid mixture of amides was separated by column chromatography on silica gel using chloroform–ethyl acetate (1:1) as solvent. The less polar amide A was a derivative of (*aR*)-**15**, while the more polar amide B was derived from (*aS*)-**15** (see ref 11 for absolute configuration determination).

Amide A (derivative of (*aR*)-**15**): mp 168–170 °C; $[\alpha]^{24}_{546}$ −133.9° (*c* 1, $CHCl_3$); ^1H NMR δ 1.50 (d, *J* = 7 Hz, 3 H), 1.65–2.00 (m, 10 H), 2.23 (br s, 1 H), 2.51 (br s, 1 H), 4.30 (br s, 1 H), 5.15 (quintet, *J* = 7 Hz, 1 H), 5.48 (s, 1 H), 5.80 (br d, *J* = 7 Hz, 1 H), 7.20–7.45 (m, 5 H); ^{13}C NMR 21.88, 30.55, 33.65, 37.80, 38.78, 42.61, 44.58, 45.67, 46.32, 48.50, 67.74, 112.35, 126.21, 127.30, 128.67, 143.49, 163.55, 165.79 ppm. Anal. Calcd for $C_{20}H_{25}O_2N$: C, 77.14; H, 8.09; N, 4.50. Found: C, 77.24; H, 8.12; N, 4.59.

Amide B (derivative of (*aS*)-**15**): mp 206–207 °C; $[\alpha]^{24}_{546}$ −123.2° (*c* 0.85, $CHCl_3$); ^1H NMR, peak positions identical with those of amide A; ^{13}C NMR 21.88, 30.54, 33.65, 37.76, 38.72, 42.60, 44.61, 45.70, 46.37, 48.49, 67.75, 112.33, 126.22, 127.28, 128.65, 143.50, 163.56, 165.76. Anal. Calcd for $C_{20}H_{25}O_2N$: C, 77.14; H, 8.09; N, 4.50. Found: C, 77.05; H, 8.06; N, 4.53. HPLC analysis of the amide prepared from the resolved methyl ester on a Supelco column using 50% acetonitrile–50% H_2O gave ratio A:B = 10:90, i.e., 80% ee.

(*aS*)-(5-Hydroxy-2-adamantylidene)ethanol. Ester **16** (1.31 g, 5.9 mmol) in anhydrous diethyl ether (5 mL) was added at 0 °C to a mixture of 95% $LiAlH_4$ (0.71 g) in diethyl ether (15 mL) and $AlCl_3$ (0.78 g) in diethyl ether (10 mL). After 3 h the mixture was treated carefully with 2 N NaOH and extracted with diethyl ether. The extracts were dried and evaporated to give the diol (1.12 g, 97% yield). The analytical sample was crystallized from CH_2Cl_2–hexane; mp 101–102 °C; ^1H NMR δ 1.5–1.9 (m, 12 H), 2.24 (br s, 1 H), 1.57 (br s, 1 H), 3.06 (br s, 1 H), 4.12 (d, *J* = 7 Hz, 2 H), 5.36 (t, *J* = 7 Hz, 1 H).

(*aS*)-(5-Hydroxy-2-adamantylidene)acetaldehyde (17). The diol (585 mg, 3mmol) in dichloromethane (40 mL) was stirred in an ice bath with MnO_2 (3.5 g) for 2.5 h. MnO_2 was filtered off and the aldehyde **17** after evaporation of CH_2Cl_2 was subjected to purification by radial chromatography (dichloromethane–25% diethyl ether): yield 542 mg (94%); mp 78–80 °C; $[\alpha]^{25}_{546}$ +16.5° (*c* 1, CH_2Cl_2); IR 3300, 1675, 1640 cm^{-1}; ^1H NMR δ 1.54 (s, 1 H), 1.80–2.05 (m, 10 H), 2.32 (br s, 1 H), 2.73 (br s, 1 H), 3.80 (br s, 1 H), 5.84 (d, *J* = 8 Hz, 1 H), 10.02 (d, *J* = 8 Hz, 1 H); UV ε 62 (343 nm), 21 300 (233 nm); CD Δε +0.78 (345 nm), +0.44 (254 nm), −4.2 (231 nm). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39. Found: C, 75.06; H, 8.41.

(*aS*)-(5-Hydroxy-2-adamantylidene)propene (19). Dry triphenylmethylphosphonium bromide (2.14 g, 6mmol) in THF (25 mL) was treated in a CCl_4/dry ice bath with 2.4 mL of 2.5 M BuLi in hexane. To the yellow solution after 0.5 h was added a solution of aldehyde **17** (212 mg, 1.1 mmol) in THF (3 mL). The mixture was stirred for 5 h and quenched with water. Extraction with diethyl ether gave diene **19**, which was purified by radial chromatography (dichloromethane): yield 200 mg (95%); mp 87–88 °C; $[\alpha]^{25}_{546}$ −9.2° (*c* 0.9, cyclohexane); IR (Nujol) 3260, 3080 (w), 3040 (w), 1660 (w), 1605 (w), 1165, 1150, 960 cm^{-1}; ^1H NMR δ 1.35 (s, 1 H), 1.6–1.9 (m, 10 H), 2.29 (br s, 1 H), 2.57 (br s, 1 H), 3.20 (br s, 1 H), 4.99 (dd, *J* = 11, 2 Hz, 1 H), 5.13 (dd, *J* = 16.5, 2 Hz, 1 H), 5.78 (d, *J* = 11 Hz, 1 H), 6.58 (sextet, *J* = 16.5, 11, 11 Hz, 1 H); UV ε 31 600 (238 nm); CD Δε −1.4 (208 nm). Anal. Calcd for $C_{13}H_{18}O$: C, 82.05; H, 9.54. Found: C, 82.11; H, 9.54.

(*aS*)-(5-((*tert*-Butyldimethylsilyl)oxy)-2-adamantylidene)acetaldehyde (18). This product was obtained along with **17** when the $LiAlH_4$–$AlCl_3$ reduction–MnO_2 oxidation sequence was repeated with partially *tert*-butyldimethylsilylated ester **16** (see preparation of **20** below). Separation of **18** from **17** was easily carried out by radial chromatography (dichloromethane). ^1H NMR: δ 0.09 (s, 6 H), 0.85 (s, 9 H), 1.8–2.0 (m, 10 H), 2.27 (br s, 1 H), 2.69 (br s, 1 H), 3.75 (br s, 1 H), 5.81 (d, *J* = 9 Hz, 1 H), 10.00 (d, *J* = 9 Hz, 1 H); UV ε 21 000 (233 nm); CD Δε +0.76 (346 nm).

(*aS*)-(5-((*tert*-Butyldimethylsilyl)oxy)-2-adamantylidene)propene (20). Diene **19** (86 mg, 0.45 mmol) in dichloromethane (1 mL) was stirred with imidazole (100 mg, 1.5 mmol) and *tert*-butyldimethylsilyl chloride (180 mg, 1.2 mmol) for 11 days. The mixture was filtered through silica gel using dichloromethane as solvent, and the crude product was purified by radial chromatography (hexane): yield 70 mg (51%); $[\alpha]^{25}_{546}$ −9.5° (*c* 1, cyclohexane); IR (film) 3070 (w), 3030 (w), 2930, 2850, 1660 (w), 1605 (w), 1480–1250, 1140, 1025, 910, 860, 845, 780 cm^{-1}; ^1H NMR: δ 0.06 (s, 6 H), 0.85 (s, 9 H), 1.6–1.9 (m, 10 H), 2.19 (br s, 1 H), 2.52 (br s, 1 H), 3.15 (br s, 1 H), 4.97 (dd, *J* = 11, 2 Hz, 1 H), 5.12 (dd, *J* = 16.5, 2 Hz, 1 H), 5.76 (d, *J* = 11 Hz, 1 H), 6.57 (sextet, *J* = 16.5, 11, 11 Hz, 1 H); UV ε 31 100 (238 nm); CD Δε −2.0 (230 nm), +2.0 (207 nm).

(*aS*)-(5-Hydroxy-2-adamantylidene)acetone (21). Aldehyde **17** (170 mg, 0.88 mmol) in THF (5 mL) was treated at 0 °C with 5 mL of 1.16 M MeLi. After 1 h water was added and the solution was evaporated. The residue was extracted with diethyl ether and CH_2Cl_2, and the extracts were dried over $MgSO_4$ and evaporated. The mixture of carbinols (180 mg) was dissolved in CH_2Cl_2 (15 mL) and stirred overnight with MnO_2 (1.5 g). The solution was filtered and the ketone **21** was purified by radial chromatography (CH_2Cl_2–10% diethyl ether): yield 120 mg (66%); mp 89–92 °C; $[\alpha]^{25}_{546}$ +3.0° (*c* 1.5, CH_2Cl_2); IR (Nujol) 3260, 1680, 1620, 1100 cm^{-1}; ^1H NMR δ 1.60 (s, 1 H), 1.7–1.9 (m, 10 H), 2.20 (s, 3 H), 2.25 (br s, 1 H), 2.53 (br s, 1 H), 4.21 (br s), 5.99 (s, 1 H); UV ε 65 (330 nm), 19 600 (236.5 nm); CD Δε −0.12 (337 nm), +4.3 (239 nm). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.70; H, 8.80.

(*aS*)-(5-(Hydroxymethyl)-2-adamantylidene)acetic Acid (22). NaH (6.5 g, 0.135 mol; 50% in mineral oil) was washed under nitrogen with pentane and suspended in dry dimethoxyethane (200 mL). The mixture was stirred in an ice bath while trimethyl phosphonoacetate (24.5 mL, 0.15 mol) was slowly added. After 0.5 h ketone **14** (22.5 g, 0.125 mol) in dimethoxyethane (100 mL) was added. The mixture was stirred overnight and decomposed with water. The racemic product was obtained by extraction with diethyl ether and it was directly saponified by overnight stirring at room temperature with a mixture of 2 N NaOH (125 mL) and methanol (40 mL). After the methanol was distilled off, the solution was extracted with diethyl ether, and the water phase was added dropwise to 2 N HCl (125 mL). The racemic acid was obtained as a colorless solid: mp 164–165 °C; yield 20.0 g (72%). The acid was resolved by crystallization of its salt with (*S*)-(−)-α-methylbenzylamine from methanol–acetonitrile (1:4) solution. Four crystallizations afforded the salt, mp 177–179 °C, from which the acid was obtained in the conventional way with the overall yield 27%: mp 189–191 °C; $[\alpha]^{25}_{546}$ −28.5° (*c* 1, ethanol); IR (Nujol) 3430, 3150–2450, 1695, 1645, 1390, 1265, 1240, 1185, 1030 cm^{-1}; ^1H NMR (CD_3OD) δ 1.5–2.0 (m, 10 H), 2.06 (br s, 1 H), 2.40 (br s, 1 H), 3.14 (s, 2 H), 4.08 (br s, 1 H), 4.84 (br s, 2 H), 5.58 (s, 1 H). Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.07; H, 8.07.

Methyl (*aS*)-(5-(Hydroxymethyl)-2-adamantylidene)acetate (23). Ester **23** was prepared from acid **22** by methylation with ethereal diazomethane. An analytical sample (colorless oil) was obtained by radial chromatography (hexane–diethyl ether, 1:1): $[\alpha]^{25}_{547}$ −21.1° (*c* 1, $CHCl_3$); IR (film) 3400, 2980 (w), 2910, 2850, 1715, 1650, 1480–1200, 1170, 1040; ^1H NMR δ 1.5–1.9 (m, 1 H), 2.10 (br s, 1 H), 2.52 (br s, 1 H), 3.24 (s, 2 H), 3.69 (s, 3 H), 4.14 (br s, 1 H), 5.61 (s, 1 H); UV ε 17 700 (223 nm); CD Δε −0.35 (254 nm), −0.40 (226 nm). Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 70.93; H, 8.68.

Amide of (5-(Hydroxymethyl)-2-adamantylidene)acetic Acid with (*S*)-(−)-α-Methylbenzylamine. This amide was prepared from ester **23** under conditions used for preparation of the amide of (5-hydroxy-2-adamantylidene)acetic acid (vide supra). HPLC analysis under conditions used for **15** gave 90% ee: ^1H NMR δ 1.51 (d, *J* = 7 Hz, 3 H), 1.55–1.90 (m, 10 H), 2.08 (br s, 1 H), 2.43 (br s, 1 H), 3.24 (s, 2 H), 4.18 (br s, 1 H), 5.16 (quintet, *J* = 7 Hz, 1 H), 5.48 (s, 1 H), 5.62 (br d, *J* = 7 Hz, 1 H), 7.20–7.45 (m, 5 H).

Methyl (*aS*)-(5-((Tosyloxy)methyl)-2-adamantylidene)acetate. Hydroxy ester **23** (2.36 g, 10 mmol) was dissolved in dichloromethane (10 mL) and pyridine (2 mL). After addition of *p*-toluenesulfonyl chloride (2.3 g, 12 mmol) the reaction mixture was stirred at room temperature for 4 days. The mixture was extracted with diethyl ether, washed with 2 N HCl and saturated $NaHCO_3$, dried over $MgSO_4$, and evaporated. The residue was dissolved in dichloromethane and passed through a short column of silica gel (to remove the small amount of starting material), using CH_2Cl_2 as solvent. The yield of tosylate was 3.70 g (95%). An analytical sample was purified by radial chromatography (hexane–25% diethyl ether): $[\alpha]^{25}_{546}$ −24.9° (*c* 1, cyclohexane); IR (film) 3020 (w), 2920, 2850, 1715, 1655, 1600 (w), 1500 (w), 1460, 1370, 1180, 980, 965, 860, 840, 825, 670 cm^{-1}; ^1H NMR δ 1.40–1.95 (m, 10 H), 2.07 (br s, 1 H), 2.46 (s, 3 H), 2.48 (br s, 1 H), 3.59 (s, 2 H), 3.68 (s, 3 H), 4.10 (br s, 1 H), 5.59 (s, 1 H), 7.35 (d, *J* = 8 Hz, 2 H), 7.77 (d, *J* = 8 Hz, 2 H); UV ε 29 600 (223 nm); CD Δε −0.72 (247 nm), −1.7 (228 nm), +0.2 (218 nm). Anal. Calcd for $C_{21}H_{26}O_5S$: C, 64.59; H, 6.71. Found: C, 64.58; H, 6.48.

(*aS*)-(5-Methyl-2-adamantylidene)ethanol (24). To a solution of 0.69 g (17.3 mmol of 95% $LiAlH_4$ in 15 mL of THF was added at 0 °C a solution of 0.77 g (5.77 mmol) of anhydrous $AlCl_3$ in 12 mL of THF. After 1 h of stirring, to this AlH_3 reagent was added a solution of the tosylate (2.25 g, 5.77 mmol) in THF (6 mL). Stirring was continued overnight at room temperature, followed by reflux with an additional 1.0 g of $LiAlH_4$ (6 h, added in two portions). The mixture was decomposed carefully with 2 N NaOH and extracted with diethyl ether to give crude product, which was dissolved in CH_2Cl_2 and filtered through silica gel. The yield of **24** was 0.975 g (88%). An analytical sample was obtained by radial chromatography (hexane–10% diethyl ether): $[\alpha]^{25}_{546}$ −0.9° (*c* 1, CH_2Cl_2); IR (film) 3310, 2950, 2840, 1675, 1460, 1140–930 cm^{-1}; ^1H NMR δ 0.80 (s, 3 H), 1.3–1.8 (m, 10 H), 2.02 (br s, 1 H), 2.40 (br s, 1 H), 2.90 (br s, 1 H), 4.13 (d, *J* = 7 Hz, 2 H), 5.34 (t, *J* = 7 Hz, 1 H). Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.01; H, 10.66.

Reductions of the tosylate with Super Hydride in THF or with $LiAlH_4/AlCl_3$ at room temperature resulted only in the reduction of the ester moiety: ^1H NMR δ 1.3-1.9 (m, 10 H), 2.06 (br s, 1 H), 2.45 (br s, 1 H), 2.46 (s, 3 H), 2.92 (br s, 1 H), 3.58 (s, 2 H), 4.11 (d, J = 7 Hz, 2 H), 5.34 (t, J = 7 Hz, 1 H), 7.32 (d, J = 8 Hz, 2 H), 7.76 (d, J = 8 Hz, 2 H).

(*aS*)-(5-Methyl-2-adamantylidene)acetaldehyde (25). Alcohol **24** was oxidized with MnO_2 in dichloromethane in the usual manner; the yield of aldehyde **25** was 97%. An analytical sample was purified by radial chromatography (hexane-5% diethyl ether): $[\alpha]^{25}_{546}$ -4.4° (c 1, cyclohexane); IR (film) 2910, 2850, 1675, 1630, 1460, 1210, 1140, 950 cm^{-1}; ^1H NMR δ 0.84 (s, 3 H), 1.50-1.95 (m, 10 H), 2.10 (br s, 1 H), 2.57 (br s, 1 H), 3.64 (br s, 1 H), 5.82 (d, J = 8 Hz, 1 H), 10.02 (d, J = 8 Hz, 1 H); UV ϵ 66 (345 nm), 20600 (236.5 nm); CD $\Delta\epsilon$ +0.13 (345 nm), -1.9 (235 nm). Anal. Calcd for $C_{13}H_{18}O$: C, 82.05; H, 9.53. Found: C, 82.05; H, 9.44.

(*aS*)-(5-Methyl-2-adamantylidene)propene (26). This compound was prepared from aldehyde **25** according to the procedure for preparation of **19** (diethyl ether was used as solvent instead of THF). The yield, after purification by radial chromatography (hexane), was 57%: $[\alpha]^{25}_{546}$ -3.5° (c 1, cyclohexane); IR (film) 3070 (w), 3030 (w), 2900, 2840, 1650, 1600 (w), 1460, 990, 900 cm^{-1}; ^1H NMR δ 0.78 (s, 3 H), 1.4-1.8 (m, 10 H), 2.02 (br s, 1 H), 2.41 (br s, 1 H), 3.05 (br s, 1 H), 4.94 (dd, J = 11, 2 Hz, 1 H), 5.10 (dd, J = 16.5, 2 Hz, 1 H), 5.77 (d, J = 11 Hz, 1 H), 6.62 (sextet, J = 16.5, 11, 11 Hz, 1 H); UV ϵ 30600 (240 nm); CD $\Delta\epsilon$ -0.45 (236 nm). Anal. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.13; H, 10.67.

(*aS*)-(5-Methyl-2-adamantylidene)acetone (27). Aldehyde **25** (0.38 g, 2 mmol) in dry diethyl ether (5 mL) was treated at 0 °C with 3 mL of 1.6 M MeLi. After 1 h the reaction was quenched with water, and the products were extracted with diethyl ether. The crude mixture of methylcarbinols (0.39 g) was dissolved in hexane (35 mL) and oxidized with MnO_2 (3.5 g) for 2 h. The solution was filtered and evaporated. The residual oil was purified by radial chromatography (hexane-5% diethyl ether). The yield of **27** was 0.33 g (81%): $[\alpha]^{25}_{546}$ -10.9° (c 1.4, cyclohexane); IR (film) 2900, 2840, 1690, 1460, 1360, 1180, 950 cm^{-1}; ^1H NMR δ 0.80 (s, 3 H), 1.5-1.9 (m, 10 H), 2.03 (br s, 1 H), 2.18 (s, 3 H), 2.37 (br s, 1 H), 4.06 (br s, 1 H), 5.97 (s, 1 H); UV ϵ 79 (327 nm), 15400 (240 nm); CD $\Delta\epsilon$ -0.031 (332 nm), -0.8 (240 nm). Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.35; H, 9.94.

Methyl (*aS*)-(5-Methyl-2-adamantylidene)acetate (28).[16] Aldehyde **25** (228 mg, 1.2 mmol) was dissolved in *tert*-butyl alcohol (25 mL) and 2-methyl-2-butene (6 mL). A solution of sodium dihydrogen phosphate (1.0 g, 8.3 mmol) and 80% sodium chlorite (1.25 g, 11 mmol) in water (10 mL) was added dropwise over a 10-min period. The reaction mixture was stirred overnight at room temperature. After removal of volatiles in vacuo the residue was dissolved in water (30 mL) and extracted with hexane. The aqueous layer was acidified (pH 3) with 2 N HCl and extracted with diethyl ether. The ethanol solution was washed with water, dried, and treated with ethereal diazomethane. The ester **28** was purified by radial chromatography (hexane-1% diethyl ether): yield 175 mg (67%); $[\alpha]^{25}_{546}$ -14.4° (c 1, cyclohexane); IR (film) 2900, 2840, 1720, 1650, 1460, 1440, 1395, 1245, 1230, 1170, 1040, 875 cm^{-1}; ^1H NMR δ 0.82 (s, 3 H), 1.45-1.90 (m, 10 H), 2.04 (br s, 1 H), 2.46 (br s, 1 H), 3.70 (s, 3 H), 4.07 (br s, 1 H), 5.59 (s, 1 H); UV ϵ 17200 (224 nm); CD $\Delta\epsilon$ -0.27 (253 nm), -0.5 (227 nm). Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.20; H, 9.05.

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Exciton Effects in Chiral Planar 1,3-Dienes and α,β-Unsaturated Carbonyl Compounds. Configurational Application

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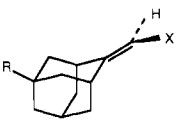
Abstract: A new application of exciton coupling between a benzoate chromophore and planar 1,3-diene as well as α,β-unsaturated carbonyl chromophore (aldehyde, ketone, or ester) for determination of the absolute configuration of axially dissymmetric molecules is reported. The effect of Z/E configuration of the chromophore on exciton interaction is noted.

Exciton coupling in circular dichroic spectroscopy,[1] which depends on Davydov splitting of excitations in two-chromophoric systems,[2] is based on the pioneering work of Kuhn[3] and Kirkwood.[4] It has found numerous applications in structural organic chemistry due largely to the extensive work of Nakanishi and Harada.[5] The scope of applications covers vicinal and distant dibenzoate and tribenzoate systems, biaromatic and heteroaromatic systems, and systems having two different chromophores whose $\pi-\pi^*$ transition excitations are close in energy. CD exciton chirality has been used, with confidence, to establish absolute configurations of molecules and rivals the Bijvoet X-ray method as a nonempirical means of doing so.[5]

We have found this method extremely useful for determining absolute configuration of compounds possessing so-called "axial dissymmetry" (Charts I and II, R = OCOPh, X = CH=CH_2, CHO, COOMe, COMe), where the two chromophores, the benzoate chromophore and a conjugated diene or conjugated

Chart I



(aS)-(-)-1, R=OH, X=COOMe
(aS)-(-)-2, R=OCOPh, X=COOMe
(aS)-(+) 3, R=OH, X=CHO
(aS)- 4, R=OH, X=CH_2OH
(aS)-(-)- 5, R=OCOPh, X=CH_2OCOPh
(aS)- 6, R=OCOPh, X=CH_2OH
(aS)-(-)- 7, R=OCOPh, X=CHO
(aS)-(-)-8, R=OH, X=CH=CH_2
(aS)-(-)-9, R=OCOPh, X=CH=CH_2
(aS)-(+)-10, R=OH, X=COMe
(aS)-(-)- 11, R=OCOPh, X=COMe
(aS)-(-)- 12, R=CH_2OH, X=COOMe
(aS)-(-)- 13, R=CH_2OCOPh, X=COOMe

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