Syntheses and Chiroptical Properties of 4-Substituted 2-Adamantylidene Derivatives. A New Sector Rule for Chiral 1,3-Dienes and α,β-Unsaturated Carbonyls

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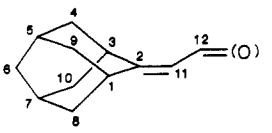
The synthesis of a series of chiral 4-axial and 4-equatorial methyl- and hydroxyl-substituted *E* and *Z* (1*R*)-2-adamantylidenepropenes and α,β-unsaturated carbonyls starting with the known (+)-*endo*-bicyclo-[3.3.1]non-6-ene-3(*R*)-carboxylic acid are described. The effects of the hydroxyl and methyl substituents on the π–π* Cotton effects are discussed. A "Sector Rule" is proposed to predict the sign of the Cotton effect for chiral 1,3-dienes and α,β-unsaturated carbonyl derivatives.

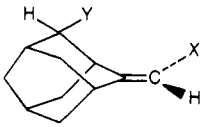
Introduction

Chiroptical properties of molecules containing cisoidal 1,3-dienes have been extensively investigated, and their long wavelength π–π* Cotton effects have been correlated with molecular structure.[1] Recently a series of chiral planar transoidal 1,3-dienes have been prepared[2] and their chiroptical properties determined. These studies resulted in the formulation of the "Planar Diene Rule"[3,2c] (Figure 1). This rule states that "after placing the transoidal 1,3-diene or α,β-unsaturated aldehyde chromophore and all atoms attached to it in a single plane as shown in Figure 1, atoms or groups of atoms falling above the plane will make a positive contribution and those falling below a negative contribution to the Cotton effect for the long wavelength π–π* transition". For cyclohexylidene derivative as shown in Figure 1, the diene as well as the 2 and 6 carbon atoms with their attached equatorial hydrogen atoms lie in the plane, and these atoms will make very little, if any, contribution to the long wavelength π–π* Cotton effect. The other atoms or groups of atoms closest to the chromophore[4] will determine the sign of the Cotton effect. Those found above the chromophore plane will make a positive contribution and those below a negative one. Thus, given the sign of the long wavelength π–π* Cotton effect one can determine the absolute configuration of the chiral planar transoidal 1,3-diene or α,β-unsaturated aldehyde. Conformational effects are important[2b,c] and the "Planar Diene Rule" would not apply to conjugated systems such as β,β-substituted and α,β-unsaturated methyl ketones or esters, since they exist largely in the cisoid conformation.[2b,c]

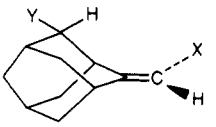
In order to avoid conformational effects due to the flexible cyclohexylidene ring,[2a-c] including ring inversion due to axial–equatorial equilibria,[5] ring-flattening, and possible chiral distortions of the ring or the chromophore[2c] by $A^{1,3}$ strain,[6] an investigation of the rigid and highly symmetrical adamantylidene system was undertaken. The chiral 5-substituted 2-adamantylideneacetaldehydes and propenes have been previously prepared[5a] and shown to obey the "Planar Diene Rule". The preparation of 4-substituted 2-adamantylideneacetaldehydes and propenes and the investigation of their chiroptical properties is the subject of this paper. The benzoates of the 4- and 5-hydroxy compounds of these two series were used in a study of exciton coupling of unlike chromophores.[5b]

Syntheses: 4(a)- and 4(e)-Hydroxy Derivatives. The 4(a)- and 4(e)-hydroxyl (Y = OH) as well as the 4(a)- and 4(e)-methyl (Y = CH_3) derivatives of the *E* and *Z* isomers of the (1*R*)-2-adamantylidene series where X = CHO and CH=CH_2 were the target molecules. They were

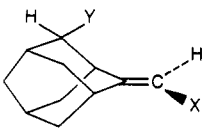




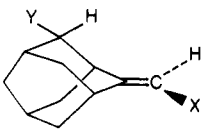
Z-(1*R*)-4(a)-**1**



Z-(1*R*)-4(e)-**2**



E-(1*R*)-4(a)-**3**



E-(1*R*)-4(e)-**4**

conveniently prepared from the known (+)-*endo*-bicyclo-[3.3.1]non-6-ene-3(R)-carboxylic acid of established absolute configuration and optical purity.[7] The acid was converted to a 5:2 mixture of (−)-(1*R*)-4(a) and (+)-4(e)-hydroxyadamantan-2-ones by the procedure of Numan and Wynberg.[7b] The epimeric ketones were separated as described by Henkel and Spector.[8]

A Wittig–Horner condensation with the axial hydroxy ketone and sodium triethyl phosphonoacetate resulted in

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(1) (a) Burgstahler, A. W.; Barkhurst, R. C.; Gawronski, J. K. In *Modern Methods of Steroid Analysis*; Heftmann, E. Ed; Academic: New York, 1973. (b) *The Molecular Basis of Optical Activity: Optical Rotatory Dispersion and Circular Dichroism*; Charney, E., Ed.; Wiley: New York, 1979. (c) *Stereochemistry: Foundamentals and Methods*; Kagan, H. B., Ed.; George Thieme: Stuttgart, 1977; Vol. 2. (d) Lightner, D. A.; Bouman, T. D.; Gawronski, J. K.; Gawronska, K.; Chappins, J. L.; Crist, B. V.; Hansen, A. E. *J. Am. Chem. Soc.* **1981**, *103*, 5314 and references cited therein.

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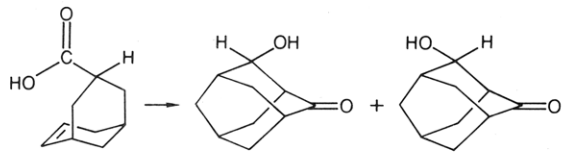


a good yield of a complex mixture of *Z*-(1*R*)-4(a)-**1** (Y = OH, X = COOEt), *E*-(1*R*)-4(a)-**3** (Y = OH, X = COOEt), and their corresponding acids. It was found convenient to saponify the crude condensation mixture and to esterify the resultant acids with diazomethane to yield a 2:3 mixture of *E* and *Z* methyl (1*R*)-4(a)-hydroxy-2-adamantylideneacetates (**1** and **3**; Y = OH, X = $COOCH_3$). The equatorial hydroxy ketone was treated in a similar manner to give a 1:1 mixture of *E* and *Z* methyl(1*R*)-4-(e)-hydroxy-2-adamantylideneacetates (**2** and **4**; Y = OH, X = $COOCH_3$). Silylation of the mixture of **1** and **3** (Y = OH, X = $COOCH_3$) with *tert*-butyldimethylsilyl chloride followed by repeated radial chromatographic separation yielded the pure silyl ether derivatives. However, desilylation with tetra-*n*-butylammonium fluoride to give pure **1** and **3** (Y = OH, X = $COOCH_3$) proved tedious; 14 days were required for the *Z* isomer and two days for the *E* isomer.

A more convenient synthesis of all four isomers **1**–**4** (Y = OH, X = $COOCH_3$), which was amenable to large scale preparation, started with the 5:2 mixture of chiral 4-axial and 4-equatorial hydroxyadamantan-2-ones. The mixture was converted to **1**–**4** (Y = OH, X = $COOCH_3$) as previously described, in 86% yield. Pyridinium chlorochromate oxidation reduced the complex mixture to a simple 5:3 mixture of methyl *Z*/*E*-(1*R*)-4-oxo-2-adamantylideneacetates, which was conducive to separation by column chromatography. Sodium borohydride reduction of (*Z*)-4-oxo isomer gave **1** (Y = OH, X = $COOCH_3$) and **2** (Y = OH, X = $COOCH_3$) in a 1:2 ratio, and reduction of (*E*)-4-oxo yielded **3** (Y = OH, X = $COOCH_3$) and **4** (Y = OH, and X = $COOCH_3$) in a 4:5 ratio, respectively.

The corresponding 4-hydroxyadamantylideneacetaldehydes (Y = OH, X = CHO) were prepared by simply reducing the (*E*)- and (*Z*)-4-oxo-2-adamantylideneacetates with AlH_3 so that each gave a mixture of glycols; *Z* gave **1** and **2** (Y = OH, X = CH_2OH) and *E* gave **3** and **4** (Y = OH, X = CH_2OH). MnO_2 oxidation of each mixture, followed by radial chromatography, yielded pure **1**–**4** (Y = OH, X = CHO).

Since all the isomers of methyl 4-hydroxy-2-adamantylideneacetate **1**–**4** (Y = OH, X = $COOCH_3$) could now be prepared conveniently, each individual isomer was converted to the corresponding derivatives by using standard procedures:[2] **1**–**4** (Y = OH, X = CHO) by AlH_3 reduction followed by MnO_2 oxidation; **1**–**4** (Y = OH, X = $CH{=}CH_2$) by reaction of the precursor aldehyde (Y = OH, X = CHO) with methylenetriphenylphosphorane; **1**–**4** (Y = OH, X = $COCH_3$) by treating the precursor aldehyde (Y = OH, X = CHO) with methylmagnesium chloride followed by MnO_2 oxidation; **1**–**4** (Y = $OSiMe_2$, *t*-Bu, X = $CH{=}CH_2$) by silylation of the corresponding alcohol (Y = OH, X = $CH{=}CH_2$).

4(a)- and 4(e)-Methyl Derivatives. The preparation of the 4-methyl-substituted 2-adamantylidene derivative (Y = CH_3) started with the same precursor that was used for the 4-hydroxy derivatives (Y = OH) namely, methyl (*Z*)- and (*E*)-(1*R*)-4-oxo-2-adamantylideneacetate. Addition of methylmagnesium chloride gave exclusively methyl (*Z*)-(1*R*)-4(e)-hydroxy-4(a)-methyl-2-adamantylideneacetate, which upon dehydration with a catalytic amount of *p*-toluenesulfonic acid in benzene yielded methyl (*Z*)-(1*R*)-4-methylene-2-adamantylideneacetate. This procedure was developed after all attempts at direct methylenation of the 4-oxo esters failed with use of the Wittig reaction and modifications thereof.

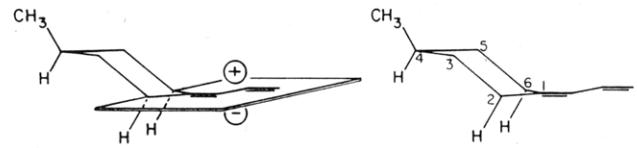
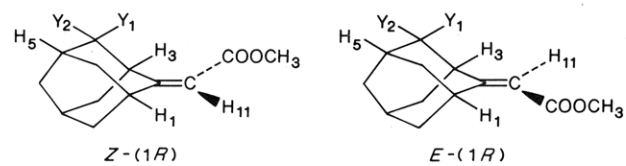


Figure 1. Planar diene rule.

Table I. ^1H NMR Data–Chemical Shifts of the Selected Protons in Methyl (*Z*)- and (*E*)-(1*R*)-4(a)- and 4(e)-Hydroxy-2-adamantylideneacetates[a]



no.	compound	H_1	H_3	$Y_1/Y_2 = H_4$	H_{11}
1	ester, $Y_1 = Y_2 = H$	2.43	4.06		5.59
2	*Z*-(1*R*)-4(a)-(−), Y_1 = OH; Y_2 = H	2.41	4.08	4.08	5.80
3	*Z*-(1*R*)-4(e)-(+), Y_1 = H; Y_2 = OH	2.40	3.85	4.05	5.64
4	*E*-(1*R*)-4(a)-(+), Y_1 = OH; Y_2 = H	4.00	2.47	4.00	5.67
5	*E*-(1*R*)-4(e)-(+), Y_1 = H; Y_2 = OH	3.84	2.45	4.00	5.63

[a] Assignment of H_1, H_3, and H_5 proton chemical shifts are based on the decoupling experiments carried out in unsubstituted methyl ester (entry 1) and benzoate derivative of *Z*-(1*R*)-4(a)-(−) ester.

The isolated exocyclic double bond was hydrogenated by using the Wilkinson catalyst,[9] chlorotris(triphenylphosphine)rhodium(I), to give a 2:1 mixture of **1** (Y = CH_3, X = $COOCH_3$) and **2** (Y = CH_3, X = $COOCH_3$), which could not be resolved. However, reduction of the mixture with AlH_3 produced a mixture of alcohols **1** and **2** (Y = CH_3, X = CH_2OH), which could be separated by radial chromatography. Oxidation of the allylic alcohols with MnO_2 yielded the corresponding α,β-unsaturated aldehydes **1** and **2** (Y = CH_3, X = CHO), which on further condensation with methylenetriphenylphosphorane afforded the dienes **1** and **2** (Y = CH_3, X = $CH{=}CH_2$). Addition of methylmagnesium chloride to the isomeric α,β-unsaturated aldehyde **1** (Y = CH_3, X = CHO) followed by MnO_2 oxidation gave the methyl ketone **1** (Y = CH_3, X = $COCH_3$) in good yield. A similar sequence of reactions was used to prepare the isomeric *E* series **3** and **4**.

Determination of Configuration. 1. Absolute Configuration. The absolute configurations of all 4-substituted 2-adamantylidene derivatives **1**–**4**, have been assigned as 1*R*, since they are derivatives of (+)-*endo*-bicyclo[3.3.1]non-6-ene-3(*R*)-carboxylic acid, whose absolute configuration has previously been determined.[7] Optical purity of all the molecules in these series is also expected to be the same as the starting acid since these molecules are not subject to racemization under the conditions of all the reactions.

2. Geometric Configurations. Each of the known[7b] (1*R*)-4(a)- and (1*R*)-4(e)-hydroxyadamantan-2-ones was

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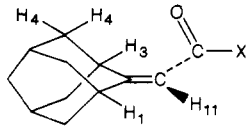
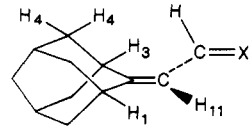
converted to a pair of *E* and *Z* isomers: 1 and 3 for the axial and 2 and 4 for the equatorial hydroxy derivative (Y = OH). Assignment of configuration has been made by ^1H and ^{13}C NMR analyses.

(a) ^1H NMR. The chemical shifts of the selected deshielded protones H_1, H_3, H_4, and H_{11} in methyl (*Z*)- and (*E*)-4(a)- and 4(e)-hydroxy-2-adamantylideneacetates have been tabulated in Table I. In the methyl 4-unsubstituted ($Y_1 = Y_2 = H$) 2-adamantylideneacetate (entry 1) the proton syn to the carbomethoxy group is expected to be deshielded due to the anisotropy of the carbonyl group, which is in a planar cisoidal configuration in the α,β-unsaturated ester[2b,c] (vide infra) and thus places the carbonyl group in the same plane as the H_3 proton as depicted.



cisoidal (X = OCH_3, CH_3)



transoidal (X = O, CH_2)

Thus the downfield proton appearing at 4.06 ppm has been assigned as H_3, and the proton at 2.43 ppm has been assigned H_1. In all the 4-substituted 2-adamantylidene derivatives the H_3 proton in the *Z* isomer and the H_1 proton in the *E* isomer will be the more deshielded proton (Table I, Experimental Section). It can be seen that the anisotropy of the ester carbonyl toward the H_3 proton found at 3.75–4.33 ppm is greater than the keto carbonyl in which H_3 is found at 3.31–3.68 ppm. The cisoidal α,β-unsaturated carbonyl, in which the oxygen of the carbonyl is pointed at H_3, is more effective than the transoidal, in which the carbon of the carbonyl is pointed at H_3, as shown by the appearance of H_3 at 3.31–3.68 ppm for all the aldehydes.[2b] The aldehyde, in turn is more effective than a carbon–carbon double bond (H_3 at 2.71–3.32 ppm) or an allylic alcohol (H_3 at 2.56–2.96 ppm).

Comparison of the chemical shifts of the 4(a) and 4(e) protons (H_4) in each pair of *Z* and *E* isomers one observes the well-established trend[10] that the axial proton appears at higher field than the equatorial proton. The chemical shift assignments of H_1, H_3, and H_4 protons have also been confirmed by decoupling experiments.

In the 4-methyl series 1–4 (Y = CH_3), in each pair of 4(a) and 4(e), the isomer with the shielded methyl group is assigned the 4(a) and the deshielded methyl is assigned the 4(e) configuration.[10,11]

(b) ^{13}C NMR. In contrast to ^1H NMR spectroscopy where one observed a variable anisotropy effect of π-bond containing substituents on the H_1 and H_3 protons, ^{13}C NMR spectroscopy disclosed that the C-1 and C-3 carbons are affected to the same extent by these substituents. The C-1 and C-3 carbons are shielded in the *E* and *Z* isomers in the order of 8 ppm, respectively. This is clearly demonstrated in Table VII (see the Experimental Section) where all the carbon resonances in (*Z*)- and (*E*)-(1*R*)-4(a)- and 4(e)-substituted-2-adamantylidene derivatives have been assigned.

The C-4 carbon resonances in these systems do not follow the well-known trend for shielding of the axial and equatorial substituent as in the normal cyclohexane ring.[12] Here, the C-4 carbon with an axial substituent is more deshielded as compared to the C-4 carbon, which is equatorially substituted. As has been previously shown[12b,13] for the 4-substituted 2-adamantanones one observes, in general, a similar deviation between the calculated and observed shielding of the C-2, C-4, and C-9 carbons in these systems. This deviation is believed to be due to the interaction of 1,3-substituents.

In going from a 4-axial to 4-equatorial substituents one can observe a clear "γ-gauche effect",[14] which can readily be used to distinguished these pairs of isomers. As can be seen in the table (Experimental Section), comparing, for example, *Z*-(1*R*)-4a-(−) and *Z*-(1*R*)-4e-(+) (entries 5 and 6), the C-9 methylene is shielded in the axial isomer whereas C-6 and C-10 are shielded in the equatorial isomer, and this observation can be clearly ascribed to the γ-effect of the C-4 substituent. This same effect is observed for each pair of isomers.

Thus by ^{13}C NMR spectroscopy one can assign the *Z* and *E* configurations by observing the shielding at C-1 and C-3, the *Z* configuration being assigned with the shielded C-3 carbon and the *E* configuration with the shielded C-1 carbon in a given set of *Z* and *E* pairs of isomers. Moreover, in each pair, the 4-axial isomer is assigned with the deshielded C-4 and C-11 and the shielded C-9 carbons whereas the 4-equatorial isomer is assigned with the shielded C-4, C-6, C-10, and C-11 carbons when the isomers are compared to each other.

3. Chromophore Conformation. The IR and UV data for the α,β-unsaturated esters, ketones, and aldehydes can be found in Table II.

It has been established[2b,c,15] that the ratio (*r*) of the integrated intensities (*I*) of the C=O and the conjugated C=C stretching frequencies can provide information concerning the conformation of the α,β-unsaturated carbonyl chromophore. A ratio (*r*) of less than 2.0 is indicative of a predominant cisoidal conformation whereas when *r* is greater than 2.0, then the conformation is predominantly transoidal. A further indication of the s-trans conformation is the $\Delta\nu$ value of the C=O and C=C frequencies. Values less than 60–70 cm^{-1} are strongly indicative of an s-trans conformation. We note in Table II that only the aldehydes (X = CHO) have *r* values (2.89–5.6) that are larger than 2.0 and $\Delta\nu$ values appreciably less (38–45 cm^{-1}) than 60 cm^{-1}, indicating that only the aldehydes have a predominantly transoidal conformation. This conclusion is consistent with the ^1H NMR findings.

The low value ($g = \Delta\epsilon\lambda/\epsilon\lambda$) of 10^{-4} for the Kuhn anisotropy factor[16] is indicative of a planar chiral chromophore. The high extinction coefficients observed for all the α,β-unsaturated carbonyls (X = $COOCH_3$, $COCH_3$, CHO) and 1,3-propenes (X = $CH{=}CH_2$) (see the Experimental Section) also speaks for a planar system.

4. Circular Dichroism. All of the compounds studied here show fairly strong Cotton effects in the 225–250-nm region; these are attributed to π–π^* transitions of the conjugated system and are presented in bold face in Tables

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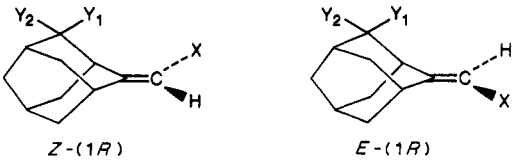
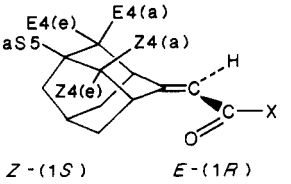
Table II. IR and UV Data of α,β-Unsaturated Esters, Ketones, and Aldehydes



no.	compound	X	$\nu_{C=O}$, cm^{-1}	I,[a] cm	$\nu_{C=C}$, cm^{-1}	I,[a] cm	$\Delta\nu$, cm^{-1}	r[b]	UV, ϵ (λ, nm)	comments
1	$Z(1R)$-4(a)-(−), Y_1 = OH; Y_2 = H	$COOCH_3$	1710	10	1650	8.6	60	1.5	14 600 (228)	planar s-cis
2	Z-(1R)-4(e)-(+), Y_1 = H; Y_2 = OH		1710[c]	10	1650[c]	7.2	60	1.6	12 900 (228)	planar s-cis
3	E-(1R)-4(a)-(+), Y_1 = OH; Y_2 = H		1718	10	1650	7.3	68	1.5	16 200 (227)	planar s-cis
4	E-(1R)-4(e)-(+), Y_1 = H; Y_2 = OH		1710[c]	10	1650[c]	6.9	60	1.7	14 670 (228)	planar s-cis
5	Z-(1R)-4(a)-(−), Y_1 = OH; Y_2 = H	$COCH_3$	1674	10	1615	11.4	59	0.9	11 000 (246)	planar s-cis
6	Z-(1R)-4(e)-(+), Y_1 = H; Y_2 = OH		1685	10	1610	11.5	75	0.8	9 300 (244)	planar s-cis
7	E-(1R)-4(a)-(+), Y_1 = OH; Y_2 = H		1682	10	1614	10.8	68	1.1	12 000 (242)	planar s-cis
8	E-(1R)-4(e)-(+), Y_1 = H; Y_2 = OH		1683	10	1611	10.4	72	0.7	12 800 (243)	planar s-cis
9	Z-(1R)-4(a)-(−), Y_1 = CH_3; Y_2 = H		1686	10	1615	10.8	71	0.8	14 800 (243)	planar s-cis
10	Z-(1R)-4(a)-(−), Y_1 = OH; Y_2 = H	CHO	1668[c]	10	1630[c]	4.5	38	4.0	17 500 (245)	planar s-trans
11	Z-(1R)-4(e)-(+), Y_1 = H; Y_2 = OH		1668[c]	10	1630[c]	4.4	38	4.5	18 500 (246)	planar s-trans
12	E-(1R-4(a)-(+), Y_1 = OH; Y_2 = H		1668[c]	10	1630[c]	3.4	38	4.7	22 900 (248)	planar s-trans
13	E-(1R)-4(e)-(+), Y_1 = H; Y_2 = OH		1668	10	1630	4.5	38	5.6	17 900 (246)	planar s-trans
14	Z-(1R)-4(a)-(−), Y_1 = CH_3; Y_2 = H		1675	10	1630	6.9	45	2.9	19 800 (237)	planar s-trans
15	Z-(1R)-4(e)-(+), Y_1 = H; Y_2 = CH_3		1665	10	1630	6.2	35	2.6	19 400 (237)	planar s-trans
16	E-(1R)-4(a)-(+), Y_1 = CH_3; Y_2 = H		1670	10	1626	5.3	44	3.6	19 000 (239)	planar s-trans
17	E-(1R)-4(e)-(+), Y_1 = H; Y_2 = CH_3		1675	10	1630	4.6	45	3.2	17 800 (238)	planar s-trans

[a] Intensity, concentration unknown in $CCl_4/CHCl_3$, and the values are corrected to the 10-cm C=O band. [b] Ratio of C=O band area to C=C band area. [c] Solvent $CHCl_3$.

Table III. CD Data[a] for Cisoid 4[b]- and 5[c]-Substituted 2-Adamantylidene Derivatives (Methyl Ketones and Methyl Esters)



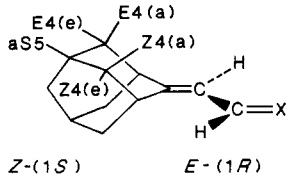
substituent	locant	$\Delta\epsilon$,[a] nm: $X = CH_3$		$X = OCH_3$	
OH	E-4(a)-(1R)	**+3.41** (240)	−4.26 (210)	**+3.62** (230)[d]	−3.85 (205)[d]
	E-4(e)-(1R)	**+1.88** (240)	+1.77 (202)	**+3.09** (228)[d]	−2.57 (202)[d]
	(a-S)-5[c]	**+4.30** (239)		**+6.0** (220)	
	Z-4(a)-(1S)*[e]	**+10.14** (249)	−10.58 (209)	**+1.61** (240)[d]	−3.81 (203)[d]
	Z-4(e)-(1S)*	**+1.45** (246)	−4.62 (215)	**+1.07** (234)[d]	−5.38 (195)[d]
				+1.36 (225)	
CH_3	(a-S)-5[c]	**−0.8** (240)		**−0.5** (227)	
	Z-4(a)-(1S)*	**+1.48** (247)	+0.64 (209)		
CH_3(a); OH(e)	E-4-(1R)			**+1.12** (230)	−2.47 (200)
	Z-4-(1S)			**+5.98** (228)	−8.28 (190)
$OSiMe_2$, t-Bu	E-4(a)-(1R)			**+6.04** (227)	−5.52 (200)
				+6.30 (221)	
	E-4(e)-(1R)			**+7.46** (225)	+5.18 (199)
					−5.60 (190)
	Z-4(a)-(1S)*			**+4.62** (233)	−5.15 (205)
	Z-4(e)-(1S)*			**+6.74** (227)	−10.01 (199)

[a] Corrected to 100% ee; cyclohexane solvent unless otherwise noted. [b] This paper. [c] Walborsky, H. M.; Gawronska, K.; Gawronski, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 6719. [d] Acetonitrile solvent. [e] Configuration reversed from that in experimental for this presentation.

III and IV. Cotton effects of similar strength are also observed at lower wavelengths in most cases and are also shown in the tables. Relatively weak Cotton effects at higher wavelengths, shown by the aldehydes and ketones, are attributed to n–π* transitions and are not given in these tables (but see the Experimental Section). For these tables, the values for the Z compounds have been reversed from those actually observed so that all would relate to the same absolute configuration.

The ketones and esters (Table III) appear to exist largely in the s-cis conformation, so that the chromophore has a plane of symmetry in which the σ bonds of all the atoms of the chromophore lie. The plane bisects the adamantane nucleus horizontally so that all of the substituents shown in the figure at the head of Table III lie above it. In every case where the substituent is oxygen there is a positive π–π* Cotton effect and in all but one of these a similar negative Cotton effect at lower wavelength (and it is not excluded for that case that such a Cotton effect would be observed at somewhat lower wavelength). The provenance of these higher energy Cotton effects is not clear; they may arise from other transitions of the conjugated chromophore. Alternatively, it will be noted that they fall in the region where end absorption due to oxygen occurs; Weig-

Table IV. CD Data[a] for Transoid 4[b]- and 5[c]-Substituted 2-Adamantylidene Derivatives (Propenes and Acetaldehydes)



Z-(1S) E-(1R)

substituent	locant	Δε, nm X = CH_2		X = O	
OH	*E*-4(a)	+1.31 (247)	−1.96 (205)	+5.87 (236)	−7.83 (214)
		+2.33 (239)	−2.33 (196)		
		+2.81 (233)		[+2.86 (241)][d]	[−2.06 (218)][d]
		+2.24 (224)			
	E-4(e)	+0.93 (245)	−1.54 (210)	+3.36 (242)[d]	−1.48 (215)[d]
		+1.93 (236)	+4.98 (190)		+1.20 (197)[d]
		+1.27 (225)			
	a-*S*	−1.4 (230)		−4.2 (231)	
	Z-4(a)*[e]	−1.31 (241)	−1.43 (216)	−0.68 (250)[d]	+1.27 (220)[d]
		−2.61 (232)	+1.79 (198)	−1.13 (244)[d]	−3.08 (195)[d]
				−0.82 (238)[d]	
	Z-4(e)*	−0.36 (248)	+0.17 (224)	−2.14 (243)[d]	+1.05 (217)[d]
		−0.48 (242)	−5.33 (190)		−4.38 (196)[d]
		−0.60 (234)			
CH_3	*E*-4(a)	+1.00 (249)	−2.48 (194)	+2.12 (238)	−2.79 (208)
		+1.64 (240)			
		+1.82 (232)			
	E-4(e)	+1.53 (248)	−0.59 (210)	+2.68 (238)	−1.50 (208)
		+2.63 (240)	+1.09 (190)		
		+1.96 (232)			
		+1.46 (225)			
	a-*S*	−0.45 (236)		−1.9 (235)	
	Z-4(a)*	−1.01 (247)	+0.86 (198)	−0.90 (236)	+2.62 (206)
		−1.58 (240)			
		−2.02 (234)			
	Z-4(e)*	−0.99 (249)	−2.64 (206)	−1.86 (236)	+0.80 (208)
		−1.24 (238)			−1.74 (194)
$OSiMe_2$, *t*-Bu	*E*-4(a)	+1.42 (240)	+0.82 (210)	+4.42 (237)	−3.44 (211)
		+1.24 (234)			
		+0.98 (227)			
	E-4(a)	+1.46 (246)	−1.11 (205)	+5.01 (238)	−1.73 (205)
		+2.36 (235)	+0.70 (190)		
		+1.80 (225)			
	a-*S*	−2.0 (230)	+2.0 (207)	−5.4 (231)	
	Z-4(a)*	+0.69 (250)		+1.48 (246)	+5.07 (210)
		+0.61 (242)			−4.64 (195)
		+0.87 (235)			
	Z-4(e)*	−0.36 (246)	−2.09 (195)	−1.71 (232)	+0.55 (211)
		−0.58 (233)			−3.68 (197)

[a] Corrected to 100% ee; cyclohexane solvent unless otherwise noted. [b] This paper. [c] Walborsky, H. M.; Gawronska, K.; Gawronski, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 6719. [d] Acetonitrile solvent. [e] Configuration reversed from that in experimental for this presentation.

ang has pointed out that a coupled oscillator mechanism for rotatory effects leads to the expectation of just such pairs of Cotton effects as the "chromophore" and "perturber" exchange roles.[17] Some support for the view that this is the case here is provided by the observation that the methyl derivatives do not follow this pattern. We provisionally suggest that α,β-unsaturated carbonyl compounds (ketones and esters) in the s-cis conformation will follow a planar sector rule such that substituents on the upper side of the chromophore, when it is oriented as shown in Figure 2, will give positive Cotton effects in the 225–250-nm region of the spectrum. This is, in essence, a helicity rule.[16b,18] The curvature of the chromophore will cause a π–π* transition to have a magnetic moment perpendicular to its plane of symmetry. Substituents on the ring that tend to increase the number or the mobility of electrons above that plane would provide an electric

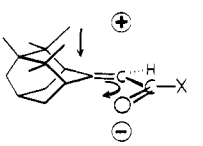


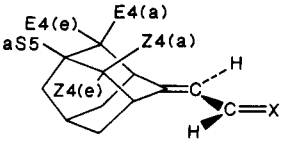
Figure 2. Planar "Sector Rule" for cisoid α,β-unsaturated carbonyl compounds. A positive π–π* Cotton effect results from the influence of a substituent above the plane of the curved chromophore.

component (along bonds that lead to the chromophore) parallel to the magnetic moment, thereby producing a positive Cotton effect. These effects are clearly seen in the 4-substituted cyclohexylidene series (lower half of Table I, ref 5a) where, presumably, the ring atoms themselves make the largest contribution (see below).

The aldehydes and dienes (Table IV) are predominantly in the s-trans conformation, in which the chromophore also has a plane of symmetry containing the σ bonds of its atoms. It was on this basis that the earlier "Planar Diene Rule" was proposed;[2c,3] it worked well with the cyclo-

(17) Weigang, O. E. *J. Am. Chem. Soc.* **1979**, *101*, 1965.
(18) Brewster, J. H. *Top. Stereochem.* **1967**, *2*, 1.

Table V. Contributions of Substituents to $\Delta\epsilon^{\pi-\pi^*}$ (R–H) in Transoid Adamantylidene Derivatives[a]



substituent		observed[a] ($\lambda \sim 235$ nm)		calculated geometric terms: Weigang equation (simple octant model)			
				atom-centered		bond-centered	
locant	R	X = CH_2	X = O	A[b]	B[b]	A[b]	B[b]
	CH_3	+1.82	+2.12				
E-(1*R*)-4(a)				−0.0030 (+0.0190)	−0.0112 (+0.0384)	−0.0015 (+0.0140)	−0.0147 (+0.0578)
	OH	+2.81	+5.87				
	CH_3	+1.96	+2.68				
E-(1*R*)-4(e)				+0.0079 (+0.0058)	+0.0208 (+0.0225)	+0.0114 (+0.0070)	+0.0351 (+0.0347)
	OH	+1.93	+3.36				
	CH_3	−0.45	−1.90				
(a-*S*)-5				+0.0087 (−0.0073)	+0.0350 (−0.0211)	+0.0063 (−0.0080)	+0.0182 (−0.0303)
	OH	−1.40	−4.20				
	CH_3	−2.02	−0.90				
Z-(1*S*)-4(a)				+0.0272 (−0.0385)	+0.0484 (−0.0162)	+0.0161 (−0.0404)	+0.0774 (−0.0561)
	OH	−2.61	−0.82				
	CH_3	−1.24	−1.86				
Z-(1*S*)-4(e)				−0.0156 (−0.0154)	−0.0184 (−0.0218)	−0.0231 (−0.0220)	−0.0353 (−0.0409)
	OH	−0.60	−2.14				

[a] Data from this paper. [b] A, origin at center of chromopnore; B, origin at sp^2 ring atom.

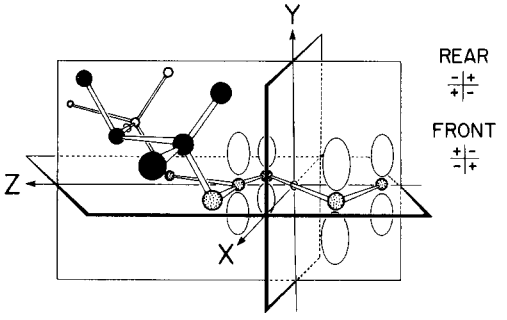


Figure 3. Provisional empirical bond-centered "Sector Rule" for transoid cyclohexylidene (and adamantylidene) compounds (upper sectors only). The transition moment lies on the *Z* axis. The *XZ* plane includes the transition moment and the stipled atoms; it lies under the atoms shown in black and white (all of which, under the earlier "Planar Diene Rule" would have made negative CD contributions). The addition of a second (*YZ*) plane intersecting along the transition moment at the center of the chromophore would make those atoms *E* to the chromophore positive contributors.

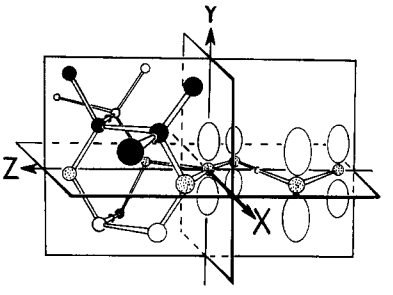
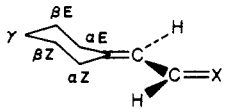


Figure 4. Provisional empirical atom-centered "Sector Rule" for transoid adamantylidene compounds. The transition moment lies on the *Z* axis; the *XZ* plane contains the σ bonds of the chromophore and the *YZ* plane contains the ends of the π system. The stipled atoms lie on the σ plane and would not contribute to optical rotation. The atoms falling in positive sectors are shown in white; those falling in negative sectors in black.

hexylidene derivatives for which it was proposed. Under that rule, it would have been expected that all of the substances shown in Table IV would show negative Cotton effects. The *E* derivatives, however, all give positive effects, as do the silyl derivatives of the axial *Z* alcohols. The results can be accommodated by a sector rule for both series that includes two additional surfaces perpendicular to the first (Figure 3; see also Figure 4). Two of these planes (here *YZ* and *XZ*) intersect along the transition moment and split the ring system unsymmetrically into four sectors, placing the upper *E* and *Z* substituents in different sectors. At least one additional surface appears to be required, at least for the diene chromophore, which has a 2-fold rotation axis perpendicular to the *XZ* plane. For simplicity, we provisionally place this surface perpendicular (*XY*) to the other two, with the origin of coordinates at the end of the chromophore nearest the substituents (atom-centered, Figure 4). Such a surface would pass close to the *Z*-a substituent so that if the latter were large (as in the silyloxy derivatives) it would cross over into a positive sector. This suggested arrangement does not preclude others- including one in which two additional *XY* planes are present, one at the center of chromophore (bond-centered, Figure 3) and one at the other end, or one in which the *XY* plane is supplemented by two conical surfaces intersecting at the center of the chromophore (following Weigang's analysis of electric dipole allowed transitions).[17] Nor does it exclude the occurrence of different rules for "inner sphere" (e.g. allylic) and "outer sphere" perturbing groups.[4]

Virtually every one of these compounds exhibits several Cotton effects of similar size in the wavelength region of 225–250 nm. For convenience in assessing relative magnitudes we take CD maxima nearest the middle of this range. On this basis it was found that the α,β-unsaturated aldehydes and dienes give Cotton effects of similar size and that methyl and hydoxyl substituents make similar contributions (Tables V). Using data for 4-*tert*-butylcycloalkylidenepropenes[3] we estimate the contribution of an axial (*E*)-(2*S*)-methyl group at $\Delta\epsilon = +3.25$, on which basis the contribution of the enantiomerically situated ring atom (β-*E*) would be $\Delta\epsilon$ −3.25 (Table VI). The contribution of the β-*Z* atom was estimated at $\Delta\epsilon$ −1.90 in a similar way. The contribution of the ring itself was estimated from values for the (*Z*)-3(*R*)-, (*E*)-3(*S*)-, and (*Z*)-2(*R*)-methylcyclohexylidenepropenes[3] by using the conformational

Table VI. Contributions of Ring Atoms and Bonds to $\Delta\epsilon^{\pi\to\pi^*}$ (C–H) in Transoid Cyclohexylidene Derivatives[a]



ring atom	bonded to	estimated contribution of atom[a]	calculated geometric terms: Weigang equation (simple octant model) atom-centered A[b]	atom-centered B[b]	bond-centered A[b]	bond-centered B[b]	ring bond
αE	βE	0	**−0.0177**	**−0.0431**			
					−0.0196 (+0.0080)	**−0.1192** (+0.0899)	αE–βE
βE	αE		−0.0160	−0.0713			
	γ		+0.0011	+0.0294			
	Σ	−3.25	**−0.0149** (+0.0073)	**−0.0419** (+0.0489)			
					−0.0073 (−0.0017)	**−0.0301** (−0.0144)	βE–γ
γ	βE		−0.0121	−0.0542			
	βZ		+0.0081	+0.0135			
	Σ	−0.94	**−0.0040** (−0.0079)	**−0.0407** (−0.0438)			
					+0.0064 (−0.0170)	**−0.0140** (−0.0825)	βZ–γ
βZ	γ		+0.0007	−0.0433			
	αZ		+0.0339	+0.0459			
	Σ	−1.90	**+0.0346** (−0.0290)	**+0.0026** (−0.0818)			
					+0.0496 (−0.0271)	**+0.0348** (−0.0872)	αZ–βZ
αZ	βZ	0	+0.0567	−0.1172			
Σ ring		−6.09	**+0.0547** (−0.0296)	**−0.2403** (−0.0767)	**+0.0291** (−0.0378)	**−0.1285** (−0.0942)	

[a] Data from this paper. [b] A, origin at center of chromophore; B, origin at sp^2 ring atom.

composition data and values for the methyl substituents: −6.09 ± 0.12. Values calculated in a similar way from the (a-*S*) and (*E*)-2(*R*)-methyl compounds deviate appreciably from this value, by equal amounts in opposite directions. The value taken for the ring contribution, taken with that for the β atoms indicates that the γ atom makes a negative contribution: $\Delta\epsilon = -0.9$. The large negative contribution of the ring itself makes it clear that the "Planar Diene Rule" reflects the orientation of the ring to the chromophore as that is dictated by the conformational requirements of the substituents. We note that the β-*E* atom does not follow the "Sector Rule" that applies to substituents on the adamantane nucleus. This could indicate that allylic substituents, being linked to the chromophore by σ bonds that overlap, to some extent, the π system itself, must be distinguished from other, more remote and less directly connected, substituents.

Substituents in the 2- and 6-positions of the cyclohexylidene moiety represent interesting examples.[2c] We have shown that with the 2,2,4,6,6-pentamethylcyclohexylidene moiety one creates a severe $A^{1,3}$-strain situation so that in the cases of the pentamethyl-substituted cyclohexylideneacetic acid and acetone derivatives the chromophore assumes a cisoidal nonplanar conformation, and the ring maintains its integrity.[2c] However, in the case of 2,2,4,6,6-pentamethylcyclohexylidenepropene and acetaldehyde derivatives, MMP2 calculations (see the Experimental Section) show that the chromophores are transoidal and planar[2c] and that the $A^{1,3}$ strain is relieved by distorting C-1 of the ring so that the chromophore bisects the methyl groups in the 2- and 6-positions. Thus, in the diene the *Z* equatorial methyl group is ~53° and the *E* equatorial group is ~48° out of the plane of the diene chromophore and correspondingly ~48° and ~50° out of the plane of the α,β-unsaturated aldehyde chromophore. Being out of the plane these groups will now make a significant contribution to the sign and the magnitude (inner sphere[4]) of the Cotton effect.

Application of the *bond-centered* "Sector Rule" (Figure 3) to (a-*S*)-(+)-2,2,4,6,6-pentamethylcyclohexylidenepropene one sees that C-3, C-4, and the E-axial methyl group on C-6 all fall into the (−)-sectors. Whereas C-5 and the *Z* axial methyl group on C-2 as well as the *E* equatorial methyl group falls into the (+)-sector. Important to note is that the *Z* equatorial methyl group falls into a (+)-sector by virtue of the fact that it extends into a front (+)-octant. The observation of a very strong Cotton effect, $\Delta\epsilon$ + 10–16 for this series of compounds[2c] is consistent with the findings of the bond-centered "Sector Rule".

Weigang[17] has presented a sector rule for electric dipole allowed transitions, which we have attempted, without success, to apply to the s-trans diene chromophore. In this model, the transition moment for the major chromophore is aligned along the *Z* axis of a right-handed coordinate system. The "optic axis" (ordinarily a bond) of the perturbing group (or minor chromophore) is then aligned by rotation around the *Z* axis until it lies in a plane parallel to the *XZ* plane; a vertical separation (Y) of the two planes is required for chirality. The angle, θ, of the projection of the minor chromophore on the *XZ* plane is read clockwise from *Z* and the distance between the centers of the chromophores is designate *R*. When these conventions are followed, the sign and magnitude of rotational strength is given by an equation in which the geometric and trigonometric variables occur in two terms:

$$R_{NK} \simeq [1/2Y(3Z^2 - R^2) \sin 2\theta - 3XYZ \sin^2 \theta]R^{-5}$$

The first of these terms gives rise to a sector rule that features a nodal surface in the *XZ* plane and a surface conical about the *Z* axis with the apices of the cones at the origin. We interpret this rule as one pertaining to perturbations of electrons along the bonds of the minor chromophore induced by changes in field strength parallel (over the ends of the chromophore) or antiparallel (over its center) to the transition moment (*Z* axis). The second term surfaces interesting normal to one another at the origin. We interpret this rule as relating to perturbations, along bonds, induced by radial changes of field strength toward, or away from the *Z* axis. Each of these rules places a nodal surface (other than *XZ*) where the other would provide a maximum effect, for a total of 16 sectors (four in the region of concern to us). In Tables V and VI we present the values calculated (geometric and trigonometric terms only) for the case where the center of the minor chromophore is an atom (e.g., C) or alternatively a bond. In each case the values were also calculated for the case

where the origin of coordinates is at the center of the chromophore (A) or at the end nearest the perturbing groups (B). Corresponding values for a simple octant rule:

$$R_{NK} \simeq (-3XYZ)R^{-5}$$

where the XZ plane contains the σ bonds and the YZ plane the terminal p orbitals of the π bonds of the chromophore are shown in parentheses. It is seen that the values calculated from the Weigang model for substituents attached by bonds essentially parallel to the π-system are always of the wrong sign (Table V); values for those groups, which are attached by bonds parallel to the σ plane, are always correct in sign. There is a nearly 6-fold spread in magnitude when the origin is centered in the chromophore (A), but a possibly more realistic spread of about three when the origin is at the near end of the chromophore (B). The atom-centered calculations for ring atoms (Table VI) require that two bonds each at β and γ atoms be taken into account; the net value for each atom under the Weigang model is shown in bold face. The orientation of the Z axis and the rotation necessary to align optic axes produces contributions by the α atoms (along their bonds to β atoms) under the Weigang model. None of the models does well for individual atoms or bonds. The Weigang model indicates a large rotation of the correct sign for the cyclohexylidene ring only when the origin of coordinates is placed at the near end of the chromophore. In all cases, the simple octant model indicates a negative rotation for the cyclohexylidene ring, but a large value only when the center of coordinates is at the near end of the chromophore. It is on this basis that we propose the simple "Sector Rule" shown in Figures 3 and 4 for cyclohexylidene and adamantylidene propenes and acetaldehydes. We interpret this result as indicating that atoms and groups not immediately attached to the atoms α to the chromophore interact with the chromophore through-space and normal to the π (XZ) plane. The difficulty with the Weigang model may simply indicate that it is not designed for the system at hand. It is clearly designed for linear and cylindrically symmetrical chromophore, which ours is not. In π systems due attention must be given to the important differences between σ and π planes. It would also appear important to take into account the special relationship of allylic bonds and substituents with the π orbitals of such systems.

Experimental Section

All melting points and boiling points are uncorrected. ^{1}H NMR spectra were recorded at 200 or 270 MHz with $CDCl_3$ as solvent unless noted otherwise, with Me_4Si and $CHCl_3$ (7.26 ppm) as internal standards.

Optical rotations were measured at the 546.1-nm mercury line on a Bendix-Ericson Model 987 ETL/NPL polarimeter equipped with a Bendix Model DR-1 digital display. The cell length was 0.4 dm, and the accuracy was ±0.002°. Ultraviolet (UV) spectra were recorded with a Cary 219 spectrophotometer. Circular dichroism (CD) spectra were recorded with JASCO Model J-500C spectrophotometer. The CD data have been corrected for the optical purities of the samples. The cell path lengths used in UV and CD measurements were 1 and 0.1 cm, respectively. All spectral grade solvents were purified and distilled before use.

Column chromatography was carried out by using either silica gel (70–230 mesh) (Merck) or activated alumina F-20 (80–200 mesh). Radial chromatography separations were performed with Merck silica gel 60 PF_{254}. High-pressure liquid chromatography (HPLC) was performed on (4.6 mm × 25 cm) Ultrasphere-Si and Pirkle covalent phenylglycine columns using 2-propanol–heptane solvent mixtures with a flow rate of 1 mL/min and a variable wavelength detector.

All bulk solvents were distilled before use. Diethyl ether, dimethoxyethane, and THF were dried by refluxing and distilling from sodium benzophenone dianion.

(1*R*)-4(e)- and (1*R*)-4(a)-Hydroxyadamantan-2-ones. Via the reported procedures[7,19] (+)-*endo*-bicyclo[3.3.1]non-6-ene-3-(*R*)-carboxylic acid of known absolute configuration was prepared. The enantiomeric excess was estimated by converting the resolved acid into the corresponding diastereomeric amides with optically pure (−)-α-phenylethylamine and separation of the amides by using analytical HPLC. 3(*R*)-*endo*-Bicyclo[3.3.1]non-6-ene-3-carboxylic acid (2.78 g, $[\alpha]^{25}_D$ +127.45 ± 0.8° (*c* 0.53, C_2H_5OH, 84% ee) was converted into mixture of (1*R*)-4(e)- and (1*R*)-4(a)-hydroxyadamantanones (2.60 g) by using the Numan and Wynberg method.[7] The two epimers were further separated by using the method described by Henkel and Spector[8] to give 1.60 g of (1*R*)-4(a)-hydroxyadamantan-2-one: $[\alpha]^{25}_{Hg}$ −14.27 ± 0.03° (*c* 1.03, dioxane); $[\alpha]^{25}_{Hg}$ −15.02 ± 0.02° (*c* 0.99, $CHCl_3$) and 0.52 g of (1*R*)-4(e)-hydroxyadamantan-2-one: $[\alpha]^{25}_D$ +5.59 ± 0.49°, $[\alpha]^{25}_{Hg}$ +5.44 ± 0.35° (*c* 1.09, dioxane); $[\alpha]^{25}_{Hg}$ +4.7 ± 0.3° (*c* 1.03, $CHCl_3$). All the spectral data were identical with those previously reported.[19,20]

***E*,*Z* Mixture of Methyl (1*R*)-4(a)-Hydroxy-2-adamantylideneacetate.** To a stirred suspension of sodium hydride (50% dispersion, 0.92 g, 2.5 equiv) in 20 mL of dry dimethoxyethane was added triethyl phosphonacetate (2.37 g, 1.1 equiv) under a nitrogen atmosphere. After the evolution of H_2 ceased, stirring was continued for 1 h. (1*R*)-4(a)-Hydroxy ketone (1.6 g, 84% ee) in 5 mL of DME was added. The reaction mixture was stirred at room temperature for another 1 h and cooled to 0 °C. Ice water was added, and the reaction mixture was acidified with dilute HCl. Mixture of products was extracted into CH_2Cl_2 (3 × 300 mL), and the combined organic fractions were concentrated to give *E*,*Z* mixture of both ethyl esters and the corresponding acids.

The above crude mixture was treated with 10 mL of 20% KOH in 10 mL of methanol at refluxing temperature for 30 min. Most of the methanol was removed under rotary evaporator, and the alkaline layer was extracted with ether (3 × 50 mL). The cooled alkaline solution was acidified with dilute HCl. The *E* and *Z* mixture of acids was extracted into CH_2Cl_2 (3 × 100 mL), and the combined CH_2Cl_2 solution was washed with water, dried, and evaporated to give 1.8 g (90%) of crude mixture.

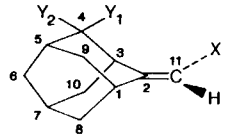
The above *E* and *Z* mixture of acids was taken in 10 mL of ether and diazomethane was added at 0 °C until the yellow color persisted. The mixture of methyl esters was filtered through 5 g of silica gel and removal of solvent gave *E* and *Z* mixture of (1*R*)-4(a)-hydroxy esters, 1.92 g, in the ratio of 4:6 (^{1}H NMR).

Methyl (*E*)- and (*Z*)-(1*R*)-4(a)-[(Dimethyl-*tert*-butylsilyl)oxy]-2-adamantylideneacetates. A solution of *E* and *Z* mixture of (1*R*)-4(a)-hydroxy esters (1.92 g), imidazole (1.76 g, 3 equiv), and dimethyl-*tert*-butylsilyl chloride (1.56 g, 1.20 equiv) in 10 mL of CH_2Cl_2 was stirred at room temperature for 3 days under N_2 atmosphere. The silyl ethers were filtered through 10 g of silica gel with 50 mL of CH_2Cl_2. The mixture of *E* and *Z* silyl ethers was subjected to repeated radial chromatography by using 100:1 hexane–ether mixture. The fractions corresponding to the pure isomers (^{1}H NMR) were collected. The yield was 1.52 g (52%) of the less polar (*Z*)-(1*R*)-4(a)-silyl ether as a colorless liquid: $[\alpha]^{26}_{Hg}$ −44.87 ± 0.07° (*c* 0.92, $CHCl_3$); IR (CCl_4) 3000–2840, 1715, and 1654 cm^{-1}; ^{1}H NMR 0.01, 0.02 (2 s, 6 H), 0.83 (s, 9 H), 1.62–2 (m, 9 H), 2.25 (br d, J = 11.7 Hz, 1 H), 2.38 (br s, 1 H), 3.64 (s, 3 H), 3.95 (br t, J = 2.2 Hz, 1 H), 4.06 (br s, 1 H), and 5.69 (s, 1 H) ppm; ^{13}C NMR see Table VII; UV (cyclohexane) λ_{226} ϵ 14 200; CD (cyclohexane) $\Delta\epsilon_{233}$ − 3.88 and $\Delta\epsilon_{205}$ +4.33. Anal. Calcd for $C_{19}H_{32}O_3Si$: C, 67.85; H, 9.47. Found: C, 67.8; H, 9.47.

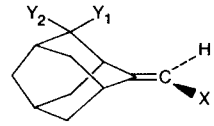
The more polar fraction yielded (0.99 g, 34%) (*E*)-(1*R*)-4(a)-silyl ether as a liquid: $[\alpha]^{25}_{Hg}$ +27.76 ± 0.04° (*c* 0.94, $CHCl_3$); IR (CCl_4) 3000–2840, 1717, and 1652 cm^{-1}; ^{1}H NMR 0.008, 0.03 (2 s, 6 H), 0.85 (s, 9 H), 1.60–2 (m, 9 H), 2.19 (br d, J = 2.2 Hz, 1 H), 2.32 (br s, 1 H), 3.67 (s, 3 H), 3.94 (br s, 1 H), 3.98 (br s, 1 H), and 5.53 (s, 1 H) ppm; ^{13}C NMR see Table VII; UV (cyclohexane) λ_{225} ϵ 15 100; CD (cyclohexane) $\Delta\epsilon_{227}$ +5.07, $\Delta\epsilon_{221}$ +5.29 and $\Delta\epsilon_{200}$ −4.64. Anal. Calcd for $C_{19}H_{32}O_3Si$: C, 67.85; H, 9.52. Found: C, 67.93; H, 9.46.

(19) Faulkner, D.; Mckervey, M. A. *J. Chem. Soc. C* **1971**, 3906.
(20) Snatzke, G.; Eckhardt, G. *Tetrahedron* **1970**, *26*, 1143; *Chem. Ber.* **1968**, *101*, 2010.

Table VII. ^{13}C NMR Data Assignment of Carbon Resonances in *Z*- and *E*-(1*R*)-4(a)- and -4(e)-Substituted 2-Adamantylidene Derivatives[a]



Z-(1*R*)



E-(1*R*)

no.	compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	others
1	adamantane[b]	28.5	37.8	28.5	37.8	28.5	37.8	28.5	37.8	37.8	37.8			
2	2-hydroxyadamantane[b]	34.7	74.7	34.7	31.2	27.8	37.8	27.3	36.7	31.2	36.7			
		(6.2)[c]	(36.9)	(6.2)	(−6.6)	(−0.7)	(0)	(−1.2)	(−1.1)	(−6.6)	(−1.1)			
3	2-hydroxy-2-methyl-adamantane[c]	39.0	73.7	39.0	34.4	27.5	38.3	27.1	32.9	34.4	32.9			
		(10.5)[c]	(35.9)	(10.5)	(−3.4)	(−1.0)	(0.5)	(−1.4)	(−4.9)	(−3.4)	(−4.9)			
4	ester, $Y_1 = Y_2 = H$	32.6	172.0	41.0	39.9	27.7	36.6	27.7	38.9	38.9	39.9			
5	*Z*-(1*R*)-4(a)-(−), Y_1 = OH; Y_2 = H	40.6	167.8	40.1	76.9	33.8	35.6	26.6	39.2	34.4	37.4	112.2	168.4	51.0 (OCH_3)
		(40.3)	(165.4)	(38.8)	(75.8)	(33.9)	(35.5)	(26.5)	(39.9)	(33.3)	(37.8)			
6	*Z*-(1*R*)-4(e)-(+), Y_1 = H; Y_2 = OH	40.0	167.3	39.9	73.7	33.6	30.2	27.2	39.7	36.4	32.4	110.1	168.9	50.9 (OCH_3)
		(39.8)	(170.9)	(38.8)	(75.8)	(33.9)	(30.0)	(27.0)	(39.9)	(38.8)	(32.3)			
7	*E*-(1*R*)-4(a)-(+), Y_1 = OH; Y_2 = H	32.5	166.7	48.3	76.9	34.3	35.8	26.7	38.8	33.2	38.8	112.1	168.0	50.9 (OCH_3)
		(31.9)	(165.4)	(47.2)	(76.8)	(33.9)	(35.5)	(26.5)	(38.9)	(32.3)	(38.8)			
8	*E*-(1*R*)-4(e)-(+), Y_1 = H; Y_2 = OH	31.6	167.3	47.8	74.4	34.0	30.2	27.2	(38.1)	35.6	33.4	110.2	169.0	50.9 (OCH_3)
		(31.4)	(170.9)	(47.2)	(76.8)	(33.9)	(30.0)	(27.0)	(38.9)	(37.8)	(33.3)			
9	*Z*-(1*R*)-4(a)-(−), Y_1 = $OCOC_6H_5$; Y_2 = H	40.4	165.6	37.0	78.9	31.9	35.7	26.7	39.4	34.9	37.6	112.0	166.7	50.7 (OCH_3), 128.2 (2 CH), 129.5 (2 CH), 130.8 (C), 132.6 (CH), 167.0 (C=O)
10	*Z*-(1*R*)-4(e)-(+), Y_1 = H; Y_2 = $OCOC_6H_5$	39.9	165.4	36.9	75.8	31.4	31.2	27.1	39.7	36.0	33.7	111.0	166.6	50.9 (OCH_3), 128.3 (2 CH), 129.6 (2 CH), 130.8 (C), 132.8 (CH), 166.6 (C=O)
11	*E*-(1*R*)-4(a)-(−), Y_1 = $OCOC_6H_5$; Y_2 = H	32.3	165.7	45.1	79.2	31.9	35.7	26.7	38.9	33.7	38.9	111.4	167.0	50.8 (OCH_3), 128.3 (2 CH), 129.6 (2 CH), 130.6 (C), 132.9 (CH), 167.7 (C=O)
12	*E*-(1*R*)-4(e)-(+), Y_1 = H; Y_2 = $OCOC_6H_5$	31.6	165.5	44.8	76.5	31.5	31.3	27.0	38.7	35.4	34.5	111.2	167.0	50.9 (OCH_3), 128.4 (2 CH), 129.6 (2 CH), 130.6 (C), 133.0 (CH), 167.0 (C=O)
13	*Z*-(1*R*)-4(a)-(−), Y_1 = $OSiMe_2$, *t*-Bu; Y_2 = H	40.8	167.1	40.3	77.0	35.2	35.9	26.8	39.9	33.9	37.6	111.3	168.9	50.4 (OCH_3), −5.2 (CH_3), −5.1 (CH_3), 25.6 (3 CH_3), 17.9 (C)
14	*E*-(1*R*)-4(a)-(+), Y_1 = $OSiMe_2$, *t*-Bu; Y_2 = H	32.5	167.1	49.0	77.4	35.2	35.8	26.8	38.9	33.1	38.8	110.9	169.5	50.6 (OCH_3), −4.7 (2 CH_3), 25.7 (3 CH_3), 18.0 (C)
15	*Z*-(1*R*)-(−), Y_1 = CH_3; Y_2 = OH	40.3	167.1	44.2	74.4	38.2	32.1	26.6	40.5	35.2	34.4	110.5	169.7	50.7 (OCH_3), 27.3 (CH_3)
		(40.0)	(167.1)	(43.1)	(74.8)	(38.2)	(31.7)	(26.3)	(40.4)	(36.5)	(34.0)			
16	*E*-(1*R*)-(+), Y_1 = CH_3; Y_2 = OH	31.8	167.1	52.7	74.4	38.1	32.2	26.6	39.6	34.6[d]	35.5[d]	110.8	169.6	50.8 (OCH_3), 27.8 (CH_3)
		(31.6)	(167.1)	(51.5)	(75.8)	(38.2)	(31.7)	(26.3)	(39.4)	(35.5)	(35.0)			
17	*Z*-(1*R*)-4(a)-(−), Y_1 = OH; Y_2 = H	40.8	173.5	40.4	76.4	34.2	35.5	27.0	39.4	33.9	38.1	124.8	190.5	
18	*Z*-(1*R*)-4(e)-(+), Y_1 = H; Y_2 = OH	40.1	173.3	40.1	74.0	34.1	30.1	27.3	39.6	35.9	33.0	122.8	190.0	
19	*E*-(1*R*)-4(a)-(+), Y_1 = OH; Y_2 = H	32.8	173.1	48.4	76.7	34.3	35.5	26.7	38.6	33.4	39.4	124.4	184.4	
20	*E*-(1*R*)-4(e)-(+), Y_1 = H; Y_2 = OH	32.0	173.1	48.0	74.0	34.0	30.1	27.3	39.2	35.9	33.3	122.8	190.1	
21	*Z*-(1*R*)-4(a)-(+), Y_1 = OH; Y_2 = H	40.0	147.0	39.9	75.8	34.9	36.0	27.2	39.1	34.0	37.4	123.4	131.7	115.8 ($CH{=}CH_2$)
22	*Z*-(1*R*)-4(a)-(−), Y_1 = $OCOC_6H_5$; Y_2 = H	39.8	147.0	36.9	78.6	32.5	35.9	27.3	39.1	34.7	37.3	121.8	132.0	115.1 ($CH{=}CH_2$), 128.3 (2 CH), 129.6 (2 CH), 130.9 (C), 132.7 (CH), 166.0 (C=O)

[a] Assignment of the carbon resonances are based on the off-resonance or DEPT sequence spectra, selective methine proton decoupled off-resonance spectra carried out in compounds unsubstituted ester and benzoate (entries 4 and 9), and comparing with the calculated shieldings (values in the parentheses, entries 5–8, 15, and 16) obtained by adding SIS in a suitable way to the shifts taken from ^{13}C NMR spectrum of unsubstituted methyl ester (entry 4); entries 4–16, X = $COOCH_3$; entries 17–20, X = CHO; entries 21–22, X = $CH{=}CH_2$. [b] Data taken from ref 13 and 22. [c] Substituent induced shifts (SIS): values in the parentheses, entries 2 and 3 calculated from $\Delta\delta(2-1)$ and $\Delta\delta(3-1)$ respectively. [d] Assignments could be interchanged.

Methyl (*Z*)-(1*R*)-4(a)-Hydroxy-2-adamantylideneacetate. A solution of the (*Z*)-(1*R*)-4(a)-silyl ether (0.2 g, 84% ee), tetra-*n*-butylammonium fluoride (1.8 mL, 3 equiv) in 2 mL of THF was stirred at 35 °C for 14 days. The mixture of products was filtered through 5 g of silica gel with 50 mL of CH_2Cl_2 and concentrated. The crude mixture was subjected to radical chromatography with hexane–ether solvent mixtures to yield two fractions: Fraction I (0.01 g) was the unreacted starting material and fraction II was solidified on standing to give 0.13 g of hydroxy ester: mp 57–59 °C; $[\alpha]^{25}_{Hg}$ −47.21 ± 0.71° (*c* 0.58, $CHCl_3$); IR (CCl_4) 3570 (sharp), 3460 (broad), 2900, 2840, 1710, and 1650 cm^{-1}; ^1H NMR 1.59 (br s, 1 H, exchangeable with D_2O, OH), 1.7–2 (m, 9 H), 2.2 (br d, *J* = 12.87 Hz, 1 H), 2.41 (br s, 1 H), 3.69 (s, 3 H), 4.08 (br s, 2 H), and 5.8 (s, 1 H) ppm; ^{13}C NMR see Table VII; UV (CH_3CN) λ_{228} ε 14600; CD (CH_3CN) $\Delta\epsilon_{240}$ −1.35 and $\Delta\epsilon_{203}$ +3.2. Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.27; H, 8.11. Found: C, 70.64; H, 8.26.

Methyl (*E*)-(1*R*)-4(a)-Hydroxy-2-adamantylideneacetate. Desilylation of 0.18 g of 84% ee (*E*)-(1*R*)-4(a)-silyl ether as above for 2 days at 25 °C gave 0.12 g, 100% yield of the hydroxy ester as a semisolid: $[\alpha]^{25}_{Hg}$ +26.13 ± 0.4° (*c* 0.45, $CHCl_3$); IR (CCl_4) 3560 (sharp), 2900, 2840, 1718, and 1650 cm^{-1}; ^1H NMR 1.43 (s, 1 H, OH), 1.6–2.2 (m, 10 H), 2.47 (br s, 1 H), 3.68 (s, 3 H), 4 (br s, 2 H), and 5.67 (s, 1 H) ppm; ^{13}C NMR see Table VII; UV (CH_3CN) λ_{227} ε 16200; CD (CH_3CN) $\Delta\epsilon_{230}$ +3.04 and $\Delta\epsilon_{205}$ −3.23. Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.27; H, 8.11. Found: C, 70.09; H, 8.07.

***E,Z* Mixture of Methyl (1*R*)-4(e)-Hydroxy-2-adamantylideneacetate.** Via an earlier procedure, 0.47 g of (1*R*)-4(e)-hydroxy ketone (84% ee) was condensed with triethyl phosphonoacetate to give after saponification and esterification, 0.44 g (70%) of a 1:1 mixture (^1H NMR) of (*E*)- and (*Z*)-(1*R*)-4(e)-hydroxy esters, which could not be separated by chromatography. The above mixture was separated by converting into the *E* and *Z* mixture of benzoates.

Methyl (*Z*)-(1*R*)-4(e)-Hydroxy-2-adamantylideneacetate. A solution of (*Z*)-(1*R*)-4(e)-benzoyloxy ester (0.24 g, $[\alpha]^{25}_{Hg}$ +50.86 ± 0.23°, 84% ee), 10 mL of 20% KOH, and 10 mL of methanol was refluxed for 30 min. After workup and esterification with CH_2N_2, the crude ester was purified to yield the hydroxy ester (0.13 g, 80%) as a semisolid: $[\alpha]^{25}_{Hg}$ +25.22 ± 0.08° (*c* 0.83, $CHCl_3$); IR ($CHCl_3$) 3630 (w, sharp), 3570 (sharp), 3400 (broad), 2980 (w), 2910, 2850, 1710, and 1650 cm^{-1}; ^1H NMR 1.5–2.4 (m, 12 H), 3.68 (s, 3 H), 3.85 (br s, 1 H), 4.05 (br s, 1 H), and 5.64 (s, 1 H) ppm; ^{13}C NMR see Table VII; UV (CH_3CN) λ_{228} ε 12900; CD (CH_3CN) $\Delta\epsilon_{260}$ +0.24, $\Delta\epsilon_{234}$ −0.9, $\Delta\epsilon_{225}$ −1.14, and $\Delta\epsilon_{195}$ +4.52. Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.27; H, 8.1. Found: C, 70.24; H, 8.18.

Methyl (*Z*)-(1*R*)-4(e)-[(Dimethyl-*tert*-butylsilyl)oxy]-2-adamantylideneacetate. Silylation of hydroxy ester (0.15 g, 84% ee) as earlier gave 0.2 g (91%) of the silyl ether as a liquid: $[\alpha]^{26}_{Hg}$ −3.75 ± 0.23° (*c* 0.89, $CHCl_3$); IR (CCl_4) 2900 (m), 1725, and 1658 cm^{-1}; ^1H NMR 0.001, 0.1 (2 s, 2 CH_3, 6 H), 0.92 (s, 9 H), 1.4–1.7 (m, 2 H), 1.75–2 (m, 5 H), 2.2–2.45 (m, 4 H), 3.68 (s, 3 H), 3.75 (br s, 1 H), 3.94 (br s, 1 H), and 5.61 (s, 1 H) ppm; UV (cyclohexane) λ_{228} ε 14900; CD (cyclohexane) $\Delta\epsilon_{256}$ +0.62, $\Delta\epsilon_{227}$ −5.66, and $\Delta\epsilon_{199}$ +8.41. Anal. Calcd for $C_{19}H_{32}O_3Si$: C, 67.85; H, 9.52. Found: C, 67.96; H, 9.51.

Methyl (*E*)-(1*R*)-4(e)-Hydroxy-2-adamantylideneacetate. Saponification and CH_2N_2 esterification of (*E*)-(1*R*)-4(e)-benzoyloxy ester (0.24 g, $[\alpha]^{25}_{Hg}$ +74.32 ± 0.31°, 84% ee) as earlier gave 0.13 g (80%) of hydroxy ester as a crystalline solid: mp 97–100 °C; $[\alpha]^{25}_{Hg}$ +40.34 ± 0.26° (*c* 0.69, $CHCl_3$); IR ($CHCl_3$) 3570 (sharp), 3400 (broad), 2900 (m), 1710, and 1650 cm^{-1}; ^1H NMR 1.5–2.4 (m, 11 H), 2.45 (br s, 1 H), 3.68 (s, 3 H), 3.84 (br s, 1 H), 4 (br s, 1 H), and 5.63 (s, 1 H) ppm; ^{13}C NMR see Table VII; UV (CH_3CN) λ_{228} ε 14670; CD (CH_3CN) $\Delta\epsilon_{228}$ +2.6 and $\Delta\epsilon_{202}$ −2.16. Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.27; H, 8.1. Found: C, 70.5; H, 8.3.

Methyl (*E*)-(1*R*)-4(e)-[(Dimethyl-*tert*-butylsilyl)oxy]-2-adamantylideneacetate. By use of a previous procedure, silylation of hydroxy ester (0.14 g, 84% ee) for 3 days gave 0.2 g (94%) of silyl ether as a solid: mp 56–59 °C; $[\alpha]^{26}_{Hg}$ +51.25 ± 0.3° (*c* 1.15, $CHCl_3$); IR (CCl_4) 2900 (m), 1725, and 1655 cm^{-1}; ^1H NMR 0.03, 0.04 (2 s, 2 CH_3, 6 H), 0.91 (s, 9 H), 1.45–1.7 (m, 2 H), 1.7–2 (m, 5 H), 2.15–2.45 (m, 4 H), 3.68 (s, 3 H), 3.75 (br s, 1 H), 3.97 (br s, 1 H), and 5.6 (s, 1 H) ppm; UV (cyclohexane) λ_{227} ε 16300; CD (cyclohexane) $\Delta\epsilon_{225}$ +6.27, $\Delta\epsilon_{199}$ +4.35, and $\Delta\epsilon_{190}$ −4.7. Anal. Calcd for $C_{19}H_{32}O_3Si$: C, 67.85; H, 9.52. Found: C, 67.75; H, 9.67.

Methyl (*E*)- and (*Z*)-(1*R*)-4-Oxo-2-adamantylideneacetates. A convenient procedure for the synthesis and separation of all the four pure 4-hydroxy methyl esters was developed by starting from (3*R*)-*endo*-bicyclo[3.3.1]non-6-ene-3-carboxylic acid. Via the Numan and Wynberg's procedure,[7] a mixture of 13 g of (1*R*)-4(e)- and (1*R*)-4(a)-hydroxyadamantanones was prepared from 14 g of (3*R*)-*endo*-bicyclo[3.3.1]non-6-ene-3-carboxylic acid, $[\alpha]^{25}_{Hg}$ +139.67 ± 0.68° (*c* 0.46, C_2H_5OH, 92% ee). The above mixture of the crude hydroxyadamantanones (13 g) was condensed with triethyl phosphonoacetate as described earlier. The reaction mixture after workup was further saponified and treated with CH_2N_2 to yield 15 g (86%) of 4-hydroxy methyl esters.

A mixture of 4-hydroxy methyl esters (4 g), in 25 mL of CH_2Cl_2, was oxidized with pyridinium chlorochromate (5.82 g, 1.5 equiv) for 4 h. The reaction mixture was diluted with 100 mL of diethyl ether and filtered through 150 g of silica gel with ether. The combined fractions were concentrated and chromatographed on silica gel column with hexane–ether. Fractions corresponding to the pure products were collected. The less polar product (1.19 g, 30%) yielded (*E*)-(1*R*)-4-oxo ester as a crystalline solid (mp 83–85 °C; $[\alpha]^{25}_{Hg}$ +184.67 ± 0.8° (*c* 0.72, $CHCl_3$), and the polar fraction (1.98 g, 50%) gave (*Z*)-(1*R*)-4-oxo ester (white solid; mp 96–97 °C; $[\alpha]^{25}_{Hg}$ −12.24 ± 0.07° (*c* 0.52, $CHCl_3$)).

Methyl (*Z*)-(1*R*)-4(e)- and -4(a)-Hydroxy-2-adamantylideneacetates. To a solution of (*Z*)-(1*R*)-4-oxo ester, (0.5 g, 92% ee) in 20 mL of absolute ethanol was added $NaBH_4$ (0.2 g) at 0 °C, and the mixture was stirred for 2 h. The reaction mixture was diluted with water and extracted with ether (3 × 50 mL). The combined ether solution was washed with water, dried (Na_2SO_4), and concentrated. The crude mixture (2:1 ratio of 4(e) and 4(a) hydroxy esters, respectively, ^1H NMR) on separation by radial chromatography gave less polar (*Z*)-(1*R*)-4(e)-hydroxy ester (275 mg, 55%) and polar (*Z*)-(1*R*)-4(a)-hydroxy ester (130 mg, 25%) as a white solid: mp 78–80 °C.

Methyl (*E*)-(1*R*)-4(e)- and -4(a)-Hydroxy-2-adamantylideneacetates. $NaBH_4$ treatment of (*E*)-(1*R*)-4-oxo ester (0.4 g) as in the previous experiment gave a 56:44 ratio of mixture (^1H NMR) of 4(e) and 4(a) hydroxy isomers, respectively. Separation and characterization yielded less polar (*E*)-(1*R*)-4-(e)-hydroxy ester (180 mg, 45% yield) and polar (*E*)-(1*R*)-4(a)-hydroxy ester (140 mg, 35% yield).

(*Z*)-(1*R*)-4(a)-Hydroxy-2-adamantylideneacetaldehyde. To a slurry of AlH_3 [freshly prepared from 0.06 g (3 equiv) of $LiAlH_4$ and 0.07 g (1 equiv) of $AlCl_3$ in 15 mL of dry ether at 0 °C for 1 h] was added a solution of 0.12 g of 84% ee hydroxy ester in 5 mL of ether, slowly at 0 °C. After 30 min, a small amount of cold water was added until all the aluminum salts were precipitated as a thick paste. The clear ether solution was filtered through anhydrous Na_2SO_4 with ether and concentrated. The crude glycol on purification by radial chromatography using hexane–ether 1:1 mixture gave 90 mg of pure glycol as a solid: mp 101–103 °C; $[\alpha]^{25}_{Hg}$ +25.91 ± 0.41° (*c* 0.53, $CHCl_3$); IR (CCl_4) 3340 (broad), 2900 (m), and 1665 (w) cm^{-1}; ^1H NMR 1.5–2.2 (m, 10 H), 2.2–2.5 (br, 2 H, 2 OH), 2.34 (br s, 1 H), 2.96 (br s, 1 H), 3.91 (dd, *J* = 7.3, 11.7 Hz, 1 H), 3.98 (br s, 1 H), 4.20 (dd, *J* = 7.3, 11.7 Hz, 1 H), and 5.69 (t, *J* = 7.3 Hz, 1 H) ppm.

The above glycol (0.24 g) in 2 mL of CH_2Cl_2 and 10 mL of hexane was treated with 1.5 g of MnO_2. After 30 min the product was filtered free of MnO_2, and the solvent was removed. On purification by radial chromatography with hexane–ether solvent mixtures there was obtained 0.23 g (97%) of hydroxy aldehyde as a white crystalline solid: mp 144–146 °C; $[\alpha]^{25}_{Hg}$ −15.18 ± 0.3° (*c* 0.45, $CHCl_3$); IR ($CHCl_3$) 3560 (sharp), 3400 (broad), 2900 (m), 1668, and 1630 (w) cm^{-1}; ^1H NMR 1.6–2.1 (m, 10 H), 2.21 (br d, *J* = 12.8 Hz, 1 H), 2.49 (br s, 1 H), 3.68 (br s, 1 H), 4.11 (br s, 1 H), 6.01 (d, *J* = 7.9 Hz, 1 H), and 10 (d, *J* = 7.9 Hz, 1 H) ppm; ^{13}C NMR see Table VII; UV (CH_3CN) λ_{366} ε 19, λ_{348} ε 50, λ_{334} ε 69, λ_{323} ε 68, and λ_{245} ε 17500, (*c* unknown, cyclohexane) λ_{380}, λ_{362}, λ_{346}, λ_{334}, λ_{320}, λ_{300}, and λ_{236}; CD (CH_3CN) $\Delta\epsilon_{365}$ −0.07, $\Delta\epsilon_{348}$ −0.14, $\Delta\epsilon_{334}$ −0.16, $\Delta\epsilon_{265}$ −0.076, $\Delta\epsilon_{250}$ +0.57, $\Delta\epsilon_{244}$ +0.95, $\Delta\epsilon_{238}$ +0.69, $\Delta\epsilon_{220}$ −1.07, and $\Delta\epsilon_{195}$ +2.59, (*c* unknown, cyclohexane) $\Delta\epsilon_{362^-}$, $\Delta\epsilon_{347^-}$, $\Delta\epsilon_{334^-}$, $\Delta\epsilon_{322^-}$, $\Delta\epsilon_{300^+}$, $\Delta\epsilon_{255^+}$, $\Delta\epsilon_{241^+}$, $\Delta\epsilon_{232^+}$, $\Delta\epsilon_{225^+}$, and $\Delta\epsilon_{210^-}$. Anal. Calcd for $C_{12}H_{16}O_2$: C, 75; H, 8.33. Found: C, 75.18; H, 8.46.

(*Z*)-(1*R*)-4(e)- and -4(a)-Hydroxy-2-adamantylideneacetaldehydes. AlH_3 reduction of methyl (*Z*)-(1*R*)-4-oxo ester (1 g, 92% ee) was carried out as in the previous experiment to give 0.75 g of the corresponding glycols as a white solid. The crude glycols were further oxidized with active MnO_2 (5 g) in 20 mL of CH_2Cl_2 for 4 h and filtered free of MnO_2. The mixture of two aldehydes was separated very conveniently by radical chromatography using hexane–ether (3:1) into two pure isomers. The less polar isomer (0.41 g, 55%) was characterized as (*Z*)-(1*R*)-4-(e)-hydroxy aldehyde: $[\alpha]^{25}_{Hg}$ +47.13 ± 0.4° (*c* 0.55, $CHCl_3$). The polar isomer (0.26 g, 35%) gave (*Z*)-(1*R*)-4(a)-hydroxy aldehyde.

(*Z*)-(1*R*)-4(a)-Hydroxy-2-adamantylidenepropene. To a stirred suspension of 1.86 g (12 equiv) of anhydrous methyltriphenylphosphonium bromide in 20 mL of dry ether cooled to −20 °C (dry ice/CCl_4) under a nitrogen atmosphere was added 3.2 mL of 1.6 M *n*-BuLi in hexane. The resulting yellow solution was stirred for 10 min. A solution of 0.1 g of 84% ee hydroxy aldehyde in 10 mL of ether was slowly added. The cooling bath was removed, and the precipitate was stirred for 30 min. Wet ether (20 mL) was added to hydrolyze the reaction. Filtration through 10 g of silica gel with ether and concentration of the ether solvent gave 0.05 g of a semisolid. Purification by radial chromatography with hexane–ether solvent mixtures gave 44 mg (45%) of pure hydroxy propene as a solid: mp 73–75 °C; $[\alpha]^{25}_{Hg}$ +25.23 ± 0.31° (*c* 0.27, $CHCl_3$); 3540 (sharp), 3440 (broad), 3065 (w), 3015 (w), 2900, 2840, 1800 (w), 1650, and 1600 (w) cm^{-1}; ^1H NMR 1.63 (d, *J* = 8.5 Hz, 1 H, OH), 1.7–2.1 (m, 10 H), 2.34 (br s, 1 H), 3.09 (br s, 1 H), 3.94 (br d, *J* = 7 Hz, 1 H, br s in D_2O exchange spectrum), 5.02 (dd, *J* = 1.8, 10 Hz, 1 H), 5.25 (dd, *J* = 1.8, 16.5 Hz, 1 H), 6.05 (d, *J* = 11 Hz, 1 H), and 6.61 (sextet, *J* = 10.3, 10.8, 16.5 Hz, 1 H) ppm; ^{13}C NMR see Table VII; UV (cyclohexane) λ_{247} ε 14 900, λ_{239} ε 23 100, and λ_{232} ε 21 500 (CH_3CN) λ_{238} ε 25 800; CD (cyclohexane) $\Delta\epsilon_{241}$ +1.1, $\Delta\epsilon_{232}$ +2.19, $\Delta\epsilon_{216}$ +1.2, and $\Delta\epsilon_{198}$ −1.5, (CH_3CN) $\Delta\epsilon_{232}$ +1.13, $\Delta\epsilon_{203}$ −0.82, and $\Delta\epsilon_{188}$ −2.52; MS(EI), *m/e* 190 (100%, $M^{\cdot+}$), 175, 161, 147, 131, 117, 105, and 91, (high resolution) calcd for $C_{13}H_{18}O$ 190.1358, found 190.1358.

(*Z*)-(1*R*)-4(a)-[(Dimethyl-*tert*-butylsilyl)oxy]-2-adamantylideneacetaldehyde. To a slurry of AlH_3 was added silyl ether ester (1.2 g, 84% ee) in 5 mL of ether at 0 °C and stirred for 30 min. On workup and purification was obtained 0.97 g (88%) of alcohol as a solid: mp 38–40 °C; $[\alpha]^{25}_{Hg}$ −3.65 ± 0.04° (*c* 1, $CHCl_3$); IR (CCl_4) 3580 (sharp), 3480 (broad), 2950–2840, and 1665 (w) cm^{-1}; ^1H NMR 0.047, 0.06 (2 s, 6 H), 0.88 (s, 9 H), 1.6 (s, 1 H, OH), 1.65–2 (m, 9 H), 2.12 (br d, *J* = 12 Hz, 1 H), 2.3 (br s, 1 H), 2.85 (br s, 1 H), 3.9 (dd, *J* = 7.3, 11.7 Hz, 1 H), 3.97 (br s, 1 H), 4.14 (dd, *J* = 7.4, 11.5 Hz, 1 H), 5.8 (t, *J* = 7.3 Hz, 1 H) ppm. Anal. Calcd for $C_{18}H_{32}O_2Si$: C, 70.13; H, 10.39. Found: 70.38; H, 10.37.

The above alcohol (0.75 g) in hexane was treated with MnO_2 for 3 h to give silyl ether aldehyde (0.63 g, 85% yield) as a white solid: mp 58–60 °C; $[\alpha]^{25}_{Hg}$ −58.98 ± 0.18° (*c* 1, $CHCl_3$); IR (CCl_4) 3000 (w), 2900 (m), 1679, and 1635 cm^{-1}; ^1H NMR 0.02, 0.04 (2 s, 6 H), 0.83 (s, 9 H), 1.5–2.1 (m, 9 H), 2.28 (br d, *J* = 12.4 Hz, 1 H), 2.45 (br s, 1 H), 3.53 (br s, 1 H), 4.03 (br s, 1 H), 5.92 (d, *J* = 8.7 Hz, 1 H), and 8.08 (d, *J* = 8.4 Hz, 1 H) ppm; UV (cyclohexane) λ_{379} ε 23, λ_{361} ε 53, λ_{345} ε 68, λ_{331} ε 63, λ_{320} ε 51, λ_{310} ε 41, λ_{299} ε 18, and λ_{239}, ε 18 300, (CH_3CN) λ_{364} ε 24, λ_{348} ε 59, λ_{333} ε 80, λ_{322} ε 82, λ_{310} ε 74, λ_{300} ε 68, and λ_{245} ε 18 200; CD (cyclohexane) $\Delta\epsilon_{378}$ −0.1, $\Delta\epsilon_{360}$ −0.23, $\Delta\epsilon_{345}$ −0.25, $\Delta\epsilon_{333}$ −0.2, $\Delta\epsilon_{246}$ −1.24, $\Delta\epsilon_{210}$ −4.26, and $\Delta\epsilon_{195}$ +3.9 (CH_3CN), $\Delta\epsilon_{364}$ −0.11, $\Delta\epsilon_{345}$ −0.28, $\Delta\epsilon_{335}$ −0.308, $\Delta\epsilon_{260}$ −0.31, $\Delta\epsilon_{250}$ −0.36, $\Delta\epsilon_{220}$ −3.4, and $\Delta\epsilon_{195}$ +4.12. Anal. Calcd for $C_{18}H_{30}O_2Si$: C, 70.59; H, 9.8. Found: C, 70.7; H, 9.97.

(*Z*)-(1*R*)-4(a)-[(Dimethyl-*tert*-butylsilyl)oxy]-2-adamantylidenepropene. Via an earlier procedure, 47 mg of 92% ee hydroxy propene was silylated to obtain 60 mg (80%) of silyl ether propene as a colorless liquid: $[\alpha]^{27}_{Hg}$ −21.23 ± 0.45° (*c* 0.23, cyclohexane); IR (film) 3060, 3014, 2900, 2820, 1780 (w), 1650, and 1600 (w) cm^{-1}; ^1H NMR 0.01 (s, 3 H), 0.03 (s, 3 H), 0.85 (s, 9 H), 1.58 (br d, *J* = 12 Hz, 1 H), 1.71–2 (m, 8 H), 2.18 (br d, *J* = 12 Hz, 1 H), 2.29 (br s, 1 H), 2.93 (br s, 1 H), 3.92 (br t, *J* = 2.7 Hz, 1 H), 4.89 (dm, *J* = 0.6, 1.8, 9.7 Hz, 1H), 5.06 (dm, *J* = 0.6, 1.8, 17.6 Hz, 1 H), 5.89 (d, *J* = 10.9 Hz, 1 H), and 6.57 (sextet, *J* = 10.5, 10.6, 16.9 Hz, 1 H) ppm; UV (cyclohexane) λ_{250} ε 17 700, λ_{242} ε 27 400, and λ_{235} ε 25 600; CD (cyclohexane) $\Delta\epsilon_{250}$ −0.64, $\Delta\epsilon_{242}$ −0.56, and $\Delta\epsilon_{235}$ −0.8, (*c* unknown, CH_3CN) $\Delta\epsilon_{250^-}$, $\Delta\epsilon_{240^-}$, $\Delta\epsilon_{230^-}$, $\Delta\epsilon_{220^-}$, $\Delta\epsilon_{200^-}$, and $\Delta\epsilon_{190^+}$; MS (EI), *m/e* 304 ($M^{\cdot+}$), 247 (95), 173, 131, 117, 91, and 75 (100), (high resolution) calcd for $C_{19}H_{32}OSi$ 304.2222, found 304.2193.

(*E*)-(1*R*)-4(a)-Hydroxy-2-adamantylideneacetaldehyde. The hydroxy ester (0.2 g, 84% ee) was reduced with AlH_3 at 0 °C as earlier. On workup and purification there was obtained 0.15 g of glycol as a solid: ^1H NMR 1.4–2.1 (m, 10 H), 2.37 (br s, 1 H), 2.8 (br s, 1 H), 3.77 (br s, 2 H, 2 OH) 3.9 (br s, 1 H), 3.96 (dd, *J* = 7.4, 11 Hz, 1 H) 4.23 (dd, *J* = 7.4, 11 Hz, 1 H), and 5.4 (t, *J* = 7.4 Hz, 1 H) ppm.

A solution of glycol (0.14 g) in CH_2Cl_2–hexane was stirred with MnO_2 for 2 h. The product on purification afforded hydroxy aldehyde as a white solid (0.13 g, 94%): mp 140–144 °C; $[\alpha]^{25}_{Hg}$ +12.9 ± 0.33° (*c* 0.45, $CHCl_3$); IR ($CHCl_3$) 3560 (sharp), 3400 (broad), 2900 (m), 1668, and 1630 cm^{-1}; ^1H NMR 1.7–2.2 (m, 9 H), 2.25 (br d, *J* = 12.7 Hz, 1 H), 2.29 (br s, 1 H, OH), 2.59 (br s, 1 H), 3.56, (s, 1 H), 4.08 (br s, 1 H), 5.87 (d, *J* = 8.3 Hz, 1 H), and 9.98 (d, *J* = 8.3 Hz, 1 H) ppm; ^{13}C NMR see Table VII; UV (cyclohexane λ_{380} ε 10, λ_{360} ε 25, λ_{347} ε 36, λ_{333} ε 36, λ_{322} ε 33, λ_{310} ε 36, λ_{290} ε 51, and λ_{248} ε 22 900, (CH_3CN) λ_{366} ε 20, λ_{349} ε 53, λ_{334} ε 70, λ_{324} ε 69, and λ_{245} ε 20 900; CD (cyclohexane) $\Delta\epsilon_{381}$ −0.009, $\Delta\epsilon_{364}$ −0.019, $\Delta\epsilon_{349}$ −0.021, $\Delta\epsilon_{335}$ −0.016, $\Delta\epsilon_{314}$ +0.05, $\Delta\epsilon_{304}$ +0.09, $\Delta\epsilon_{293}$ +0.1, $\Delta\epsilon_{286}$ +0.08, $\Delta\epsilon_{236}$ +4.93, and $\Delta\epsilon_{214}$ −6.58, (CH_3CN) $\Delta\epsilon_{365}$ −0.02, $\Delta\epsilon_{347}$ −0.046, $\Delta\epsilon_{335}$ −0.05, $\Delta\epsilon_{325}$ −0.04, $\Delta\epsilon_{288}$ +0.02, $\Delta\epsilon_{241}$ +2.43, and $\Delta\epsilon_{218}$ −1.73. Anal. Calcd for $C_{12}H_{16}O_2$: C, 75; H, 8.33. Found: C, 75; H, 8.3.

(*E*)-(1*R*)-4(e)- and -4(a)-Hydroxy-2-adamantylideneacetaldehydes. Methyl (*E*)-(1*R*)-4-oxo-2-adamantylideneacetate (1 g, 92% ee) was reduced with AlH_3 to give on workup 0.8 g of the corresponding glycols. The crude glycols on treatment with 5 g of active MnO_2 for 6 h in 20 mL of CH_2Cl_2 gave a mixture of two main products. The less polar product (0.45 g, 56%) was identified as (*E*)-(1*R*)-4(e)-hydroxy aldehyde (mp 139–141 °C), and the polar fraction gave 0.16 g (20%) of (*E*)-(1*R*)-4(a)-hydroxy aldehyde: mp 143–145 °C.

(*E*)-(1*R*)-4(a)-Hydroxy-2-adamantylidenepropene. Via an earlier procedure, methylenetriphenylphosphorane was condensed with 0.06 g of 84% ee hydroxy aldehyde. The product was isolated and purified to obtain 0.018 g (30%) of hydroxy propene as a solid: $[\alpha]^{26}_{Hg}$ +16.76 ± 3.3° (*c* 0.11, $CHCl_3$); IR (CCl_4) 3545 (sharp), 3070 (w), 3022 (w), 2900, 2840, 1800, 1650, and 1600 (w) cm^{-1}; ^1H NMR 1.5–2.1 (m, 11 H), 2.39 (br s, 1 H), 2.95 (br s, 1 H), 3.89 (br s, 1 H), 5.01 (dd, *J* = 1.98, 10 Hz, 1 H), 5.16 (dd, *J* = 1.99, 16.8 Hz, 1H), 5.86 (d, *J* = 10.9 Hz, 1 H), and 6.6 (sextet, *J* = 10.5, 10.6, 16.8 Hz, 1 H) ppm; UV (cyclohexane) λ_{248} ε 14 700, λ_{240} ε 22 700, and λ_{234} ε 21 600; CD (cyclohexane) $\Delta\epsilon_{247}$ +1.1, $\Delta\epsilon_{239}$ +1.96, $\Delta\epsilon_{233}$ +2.36, $\Delta\epsilon_{224}$ +1.88, $\Delta\epsilon_{203}$ −1.65, and $\Delta\epsilon_{190}$ −1.96; MS (EI), *m/e* 190 (100%, $M^{\cdot+}$), 175, 161, 147, 131, 117, 105, and 79, (high resolution) calcd for $C_{13}H_{18}O$ 190.1358, found 190.1358.

(*E*)-(1*R*)-4(a)-[(Dimethyl-*tert*-butylsilyl)oxy]-2-adamantylideneacetaldehyde. AlH_3 reaction of 0.8 g of silyl ether (84% ee) yielded after workup and purification 0.62 g (85%) of alcohol as a solid: mp 50–51 °C; $[\alpha]^{25}_{Hg}$ +6.01 ± 0.04° (*c* 0.89, $CHCl_3$); IR (CCl_4) 3580 (sharp), 3000–2840, and 1668 (w) cm^{-1}; ^1H NMR 0.008, 0.03 (2 s, 6 H), 0.86 (s, 9 H), 1.4 (br s, 1 H, OH), 1.5–2 (m, 9 H), 2.08 (br d, *J* = 12 Hz, 1 H), 2.25 (br s, 1 H), 2.78 (br s, 1 H), 3.87 (br s, 1 H), 4.11 (dd or m, *J* = 3.3, 7.3 Hz, 2 H), and 5.3 (t, *J* = 7.3 Hz, 1 H) ppm. Anal. Calcd for $C_{18}H_{32}O_2Si$: C, 70.13; H, 10.39. Found: C, 70.23; H, 10.47.

The alcohol (0.48 g) in 25 mL of hexane was stirred with MnO_2 for 3 h. The product was filtered free of MnO_2, concentrated, and purified to obtain 0.38 g (80%) of silyl ether aldehyde as a solid: mp 68–70 °C; $[\alpha]^{25}_{Hg}$ +23.26 ± 0.23° (*c* 1.19, $CHCl_3$); IR (CCl_4) 2940, 2920, 2850, 2740, 2700, 1677, 1630, and 1610 (w) cm^{-1}; ^1H NMR 0.01, 0.03 (2 s, 6 H), 0.84 (s, 9 H), 1.7–2.1 (m, 9 H), 2.29 (br d, *J* = 12 Hz, 1 H), 2.45 (br s, 1 H), 3.53 (br s, 1 H), 3.99 (br s, 1 H), 5.78 (d, *J* = 8.4 Hz, 1 H), and 8.05 (d, *J* = 8.4 Hz, 1 H) ppm; UV (cyclohexane) λ_{400} ε 3, λ_{379} ε 24, λ_{361} ε 53, λ_{345} ε 68, λ_{331} ε 62, λ_{320} ε 48, λ_{306} ε 33, λ_{298} ε 27, λ_{290} ε 22, and λ_{239} ε 19 000, (CH_3CN) λ_{366} ε 23, λ_{350} ε 55, λ_{334} ε 78, λ_{322} ε 80, λ_{310} ε 75, λ_{300} ε 74, and λ_{245} ε 18 900; CD (cyclohexane) $\Delta\epsilon_{400}$ −0.002, $\Delta\epsilon_{385}$ −0.006, $\Delta\epsilon_{379}$ +0.019, $\Delta\epsilon_{373}$ −0.016, $\Delta\epsilon_{368}$ −0.02, $\Delta\epsilon_{361}$ +0.03, $\Delta\epsilon_{353}$ −0.025, $\Delta\epsilon_{341}$ +0.026, $\Delta\epsilon_{339}$ −0.01, $\Delta\epsilon_{331}$ +0.02, $\Delta\epsilon_{319}$ +0.015, $\Delta\epsilon_{308}$ +0.01, $\Delta\epsilon_{298}$ +0.007, $\Delta\epsilon_{237}$ +3.71, and $\Delta\epsilon_{211}$ −2.89, (CH_3CN) $\Delta\epsilon_{365}$ −0.015, $\Delta\epsilon_{348}$ −0.028, $\Delta\epsilon_{336}$ −0.026, $\Delta\epsilon_{324}$ −0.017, $\Delta\epsilon_{300}$ +0.004, $\Delta\epsilon_{290}$ +0.009, $\Delta\epsilon_{242}$ +3.93, and $\Delta\epsilon_{213}$ −2.62. Anal. Calcd for $C_{18}H_{30}O_2Si$: C, 70.59; H, 9.8. Found: C 70.47; H, 9.78.

(*E*)-(1*R*)-4(a)-[(Dimethyl-*tert*-butylsilyl)oxy]-2-adamantylidenepropene. As in an earlier procedure, hydroxy propene (60 mg, 92% ee), was silylated to give, after radial chromatography purification with hexane, 80 mg of silyl ether propene as a liquid: $[\alpha]^{24}_{Hg}$ +0.88 ● 0.3° (*c* 0.46, $CHCl_3$), $[\alpha]^{24}_{Hg}$ +0.4 ± 0.31° (*c* 0.22, cyclohexane); IR ($CHCl_3$) 2900 (m), 1800 (w), and 1650 cm^{-1}; ^1H NMR 0.01 (s, 3 H), 0.04 (s, 3 H), 0.86 (s, 9 H), 1.58 (br d, *J* = 12 Hz, 1 H), 1.67–2 (m, 8 H), 2.13 (br d, *J* = 13 Hz, 1 H), 2.26 (br s, 1 H), 2.92 (br s, 1 H), 3.88 (br t, *J* = 2.3 Hz, 1 H), 4.9 (dm, *J* = 0.6, 1.7, 9.7 Hz, 1 H), 5.06 (dm, *J* = 0.6, 1.7, 2.4, 17.6 Hz, 1 H), 5.71 (d, *J* = 10.9 Hz, 1 H), and 6.61 (sextet, *J* = 10.5, 10.6, 16.9 Hz, 1 H) ppm; UV (cyclohexane) λ_{249} ε 17 600, λ_{242} ε 27 300, and λ_{235} ε 25 700; CD (cyclohexane) $\Delta\epsilon_{240}$ +1.31, $\Delta\epsilon_{234}$ +1.14, $\Delta\epsilon_{227}$ +0.9, and $\Delta\epsilon_{210}$ +0.82, (*c* unknown, CH_3CN) $\Delta\epsilon_{240^+}$, $\Delta\epsilon_{220^-}$, and $\Delta\epsilon_{210^+}$; MS (EI) 304 ($M^{\cdot+}$), 247 (100), 173, 145, 131, 117, 105, 91, and 75, (high resolution) calcd for $C_{19}H_{32}OSi$ 304.2222, found 304.2193.

(*Z*)-(1*R*)-4(e)-Hydroxy-2-adamantylideneacetaldehyde. The hydroxy ester (0.1 g, 84% ee) was treated with AlH_3 to obtain 0.08 g (91%) of glycol as a solid: ^1H NMR 1.4–2.3 (m, 12 H), 2.33 (br s, 1 H), 2.85 (br s, 1 H), 3.78 (br s, 1 H), 4.14 (d, *J* = 7.3 Hz, 2 H), and 5.41 (t, *J* = 7.3 Hz, 1 H) ppm.

The glycol (70 mg) in CH_2Cl_2–hexane was stirred with active MnO_2 for 30 min. Radial chromatography separation gave 5 mg (7%) of less polar (*Z*)-(1*R*)-4-oxo-2-adamantylideneacetaldehyde and 61 mg (88%) of hydroxy aldehyde as a solid: mp 134–136 °C; $[\alpha]^{26}_{Hg}$ +40.85 +0.28° (*c* 0.54, $CHCl_3$); IR ($CHCl_3$) 3630 (sharp), 3570 (sharp), 3420 (broad), 2980 (w), 2915, 2850, 2770 (w), 2750 (w), 1668, and 1630 cm^{-1}; ^1H NMR 1.5–2.7 (m, 12 H), 3.62 (br s, 1 H), 3.93 (br s, 1 H), 5.86 (d, *J* = 8.3 Hz, 1 H), and 10.01 (d, *J* = 8.3 Hz, 1 H) ppm; ^{13}C NMR see Table VII; UV (CH_3CN) λ_{370} ε 17, λ_{350} ε 53, λ_{335} ε 71, λ_{326} ε 70, and λ_{246} ε 18 500, (*c* unkown, cyclohexane) λ_{382}, λ_{363}, λ_{347}, γ_{333}, λ_{322}, λ_{310}, and λ_{240}; CD (CH_3CN) $\Delta\epsilon_{365}$ –0.1, $\Delta\epsilon_{348}$ –0.21 $\Delta\epsilon_{337}$ –0.22, $\Delta\epsilon_{325}$ –0.16, $\Delta\epsilon_{275}$ –0.03, $\Delta\epsilon_{243}$ +1.8, $\Delta\epsilon_{217}$ –0.88, and $\Delta\epsilon_{196}$ +3.68, (*c* unknown, cyclohexane) $\Delta\epsilon_{376^-}$, $\Delta\epsilon_{358^-}$, $\Delta\epsilon_{344^-}$, $\Delta\epsilon_{330^-}$, $\Delta\epsilon_{320^-}$, $\Delta\epsilon_{260^-}$, $\Delta\epsilon_{240^+}$, $\Delta\epsilon_{230^+}$, and $\Delta\epsilon_{197^+}$. Anal. Calcd for $C_{12}H_{16}O_2$: C, 75; H, 8.33. Found: C, 74.9; H, 8.5.

(*Z*)-(1*R*)-4(e)-Hydroxy-2-adamantylidenepropene. By use of an earlier procedure, 100 mg of hydroxy aldehyde (92% ee) was condensed with methylenetriphenylphosphorane. The product on purification gave 22 mg of hydroxypropene as a solid: mp 80–84 °C; $[\alpha]^{27}_{Hg}$ +51.72 ± 0.43° (*c* 0.2, cyclohexane); IR (CCl_4) 3590 (sharp), 3400 (broad), 3070, 3030, 2900, 2850, 1800, 1650, and 1600 cm^{-1}; ^1H NMR 1.2–2 (m, 9 H), 2.16 (br d, 1 H), 2.24 (br d, 1 H), 2.32 (br s, 1 H), 3 (br s, 1 H), 3.8 (br t, 1 H), 4.98 (dm, *J* = 0.5, 1.5, 2, 10 Hz, 1 H), 5.13 (dm, *J* = 1.7, 16.8 Hz, 1 H), 5.84 (d, *J* = 10.97 Hz, 1 H), and 6.61 (sextet, *J* = 10.4, 10.99, 16.87 Hz, 1 H) ppm; UV (cyclohexane) λ_{248} ε 17 200, λ_{240} ε 26 500, and λ_{234} ε 24 700; CD (cyclohexane) $\Delta\epsilon_{248}$ +0.33, $\Delta\epsilon_{242}$ +0.44, $\Delta\epsilon_{234}$ +0.55, $\Delta\epsilon_{224}$ –0.16, and $\Delta\epsilon_{190}$ +4.93; MS(EI), *m/e* 190 (100%, $M^{\cdot+}$), 175, 161, 147, 131, 105, 91, and 79, (high resolution) calcd for $C_{13}H_{18}O$ 190.1358, found 190.1358.

(*Z*)-(1*R*)-4(e)-[(Dimethyl-*tert*-butylsilyl)oxy]-2-adamantylideneacetaldehyde. The silyl ether ester (0.19 g, 84% ee) was reduced with AlH_3 (4 equiv) as described earlier. Workup and purification by radial chromatography gave 0.14 g (80%) of alcohol as a liquid: $[\alpha]^{26}_{Hg}$ +12.96 ± 0.13° (*c* 0.9, $CHCl_3$); IR ($CHCl_3$) 3580 (sharp), 3420 (broad), 2925, 2858, and 1670 (w) cm^{-1}; ^1H NMR 0.04, 0.05 (2 s, 2 CH_3, 6 H), 0.91 (s, 9 H), 1.3–1.95 (m, 9 H), 2.1–2.4 (m, 3 H), 2.7 (br s, 1 H), 3.68 (br s, 1 H), 4.1–4.15 (br m, dd in D_2O exchange spectrum, 2 H), and 5.39 (t, *J* = 7 Hz, 1 H) ppm. Anal. Calcd for $C_{18}H_{32}O_2Si$: C, 70.13; H, 10.39. Found: C, 70.28; H, 10.48.

MnO_2 oxidation of the alcohol (0.13 g) for 1 h followed by workup and purification gave 0.12 g (93%) of silyl ether aldehyde as a solid: mp 54–56 °C; $[\alpha]^{26}_{Hg}$ +12.77 ± 0.08° (*c* 0.83, $CHCl_3$); IR ($CHCl_3$), 2925, 2858, 1670, and 1630 cm^{-1}; ^1H NMR 0.05 (s, 3 H), 0.06 (s, 3 H), 0.92 (s, 9 H), 1.4–2.1 (m, 8 H), 2.27 (br d, *J* = 12.5 Hz, 1 H), 2.47 (br s, 2 H), 3.46 (br s, 1 H), 3.82 (br s, 1 H), 5.84 (d, *J* = 8.3 Hz, 1 H), and 10 (d, *J* = 8 Hz, 1 H) ppm; UV (cyclohexane) λ_{382} ε 23, λ_{364} ε 52, λ_{348} ε 66, λ_{334} ε 62, λ_{322} ε 50, λ_{310} ε 41, λ_{300} ε 34, and λ_{242} ε 17 300, (CH_3CN) λ_{370} ε 17, λ_{350} ε 55, λ_{336} ε 74, λ_{324} ε 73, and λ_{248} ε 17 600, CD (cyclohexane) $\Delta\epsilon_{380}$ –0.08, $\Delta\epsilon_{362}$ –0.18, $\Delta\epsilon_{347}$ –0.19, $\Delta\epsilon_{333}$ –0.13, $\Delta\epsilon_{320}$ –0.07, $\Delta\epsilon_{260}$ –0.51, $\Delta\epsilon_{232}$ +1.44, $\Delta\epsilon_{211}$ –0.46, and $\Delta\epsilon_{197}$ +3.09, (CH_3CN) $\Delta\epsilon_{365}$ –0.15, $\Delta\epsilon_{349}$ –0.3, $\Delta\epsilon_{337}$ –0.31, $\Delta\epsilon_{324}$ –0.23, $\Delta\epsilon_{245}$ +1.17, $\Delta\epsilon_{220}$ –1.14 and $\Delta\epsilon_{197}$ +3.03. Anal. Calcd for $C_{18}H_{30}O_2Si$: C, 70.59; H, 9.8. Found: C, 70.49; H, 9.73.

(*Z*)-(1*R*)-4(e)-[(Dimethyl-*tert*-butylsilyl)oxy]-2-adamantylidenepropene. Silylation of hydroxy propene (68 mg, 92% ee) gave after workup and purification 100 mg (92%) of silyl ether propene as a colorless liquid: $[\alpha]^{27}_{Hg}$ +16.08 ± 0.39° (*c* 0.23, cyclohexane); IR (film) 3070, 3030, 2900 (m), 1800 (w), and 1650 cm^{-1}; ^1H NMR 0.02 (s, 3 H), 0.04 (s, 3 H), 0.93 (s, 9 H), 1.4–1.55 (m, 2 H), 1.65 (br d, 1 H), 1.7–2 (m, 5 H), 2.2–2.4 (m, 3 H), 2.87 (br s, 1 H), 3.71 (br t, 1 H), 4.97 (m, *J* = 0.6, 2.5, 9.7 Hz, 1 H), 5.13 (dm, *J* = 2.5, 16.8 Hz, 1 H), 5.82 (d, *J* = 10.9 Hz, 1 H), and 6.59 (sextet, *J* = 10.5, 10.9, 16.7 Hz, 1 H) ppm; UV (cyclohexane) λ_{250} ε 17 200, λ_{242} ε 26 400, and λ_{236} ε 24 600; CD (cyclohexane) $\Delta\epsilon_{246}$ +0.34, $\Delta\epsilon_{233}$ +0.54, and $\Delta\epsilon_{195}$ +1.92; (*c* unknown, CH_3CN) $\Delta\epsilon_{243^+}$, $\Delta\epsilon_{230^+}$, and $\Delta\epsilon_{210^+}$; MS (EI), *m/e* 304 ($M^{\cdot+}$), 247 (100%), 173, 147, 131, 105, 91, and 75, (high resolution) calcd for $C_{19}H_{32}OSi$ 304.2222, found 304.2193.

(*E*)-(1*R*)-4(e)-Hydroxy-2-adamantylideneacetaldehyde. Reaction of hydroxy ester (90 mg, 84% ee) with AlH_3 as earlier gave 69 mg of glycol as a solid: ^1H NMR 1.4–2.3 (m, 12 H), 2.39 (br s, 1 H), 2.81 (br s, 1 H), 3.83 (br s, 1 H), 4.14 (d, *J* = 7.3 Hz, 2 H), and 5.4 (t, *J* = 7.3 Hz, 1 H) ppm.

The glycol (60 mg) and MnO_2 in CH_2Cl_2–hexane were stirred for 30 min. The product was filtered and concentrated to give mixture of two components. The mixture was separated to yield less polar (*E*)-(1*R*)-4-oxoadamantylideneacetaldehyde (17 mg, 28%) and 40 mg (67%) of pure hydroxy aldehyde: mp 128–132 °C; $[\alpha]^{26}_{Hg}$ +40.41 ± 0.65° (*c* 0.51, $CHCl_3$); IR (CCl_4) 3630 (sharp), 3570 (sharp), 3400 (broad), 2980 (w), 2918, 2850, 2740 (w), 1668, and 1630 cm^{-1}; ^1H NMR 1.5–2.5 (m, 11 H), 2.56 (br s, 1 H), 3.57 (br s, 1 H), 3.92 (br s, 1 H), 5.85 (d, *J* = 8 Hz, 1 H), and 10 (d, *J* = 8 Hz, 1 H) ppm; ^{13}C NMR see Table VII; UV (CH_3CN) λ_{370} ε 17, λ_{350} ε 50, λ_{336} ε 70, λ_{322} ε 80, λ_{300} ε 99, and λ_{246} ε 17 9000, (*c* unknown, cyclohexane) λ_{380}, λ_{362}, λ_{347}, λ_{333}, λ_{290}, and λ_{239}; CD (CH_3CN) $\Delta\epsilon_{364}$ –0.05, $\Delta\epsilon_{347}$ –0.097, $\Delta\epsilon_{337}$ –0.1, $\Delta\epsilon_{325}$ –0.077, $\Delta\epsilon_{280}$ +0.018, $\Delta\epsilon_{242}$ +2.82, $\Delta\epsilon_{215}$ –1.24, and $\Delta\epsilon_{197}$ +1.01, (*c* unknown, cyclohexane) $\Delta\epsilon_{380^-}$, $\Delta\epsilon_{362^-}$, $\Delta\epsilon_{341^-}$, $\Delta\epsilon_{332^-}$, $\Delta\epsilon_{290^+}$, $\Delta\epsilon_{233^+}$, and $\Delta\epsilon_{217^-}$. Anal. Calcd for $C_{12}H_{16}O_2$: C, 75; H, 8.33. Found: C, 74.8; H, 8.4.

(*E*)-(1*R*)-4(e)-Hydroxy-2-adamantylidenepropene. By use of an earlier procedure, the hydroxy aldehyde (0.22 g, 92% ee) was condensed with methylenetriphenylphosphorane to give hydroxy propene (0.15 g, 69%) as a solid: mp 90–96 °C; $[\alpha]^{27}_{Hg}$ +47.12 ± 0.27° (*c* 0.22, cyclohexane); IR (CCl_4) 3580 (sharp), 3060, 3025, 2900, 2840, 1800 (w), and 1650 cm^{-1}; ^1H NMR 1.5–2 (m, 9 H), 2.16 (br d, *J* = 11.7 Hz, 1 H), 2.25 (dq, *J* = 2.6, 12.5 Hz, 1 H), 2.39 (br s, 1 H), 2.96 (br s, 1 H), 3.84 (br t, 1 H), 4.97 (dm, *J* = 0.7, 1.9, 2.6, 10.6 Hz, 1 H), 5.13 (dm, *J* = 0.7, 1.9, 2.6, 17 Hz, 1 H), 5.82 (d, *J* = 11 Hz, 1 H), and 6.59 (sextet, *J* = 10.5, 10.6, 16.8 Hz, 1 H) ppm; UV (cyclohexane) λ_{249} ε 17 800, λ_{241} ε 27 300, and λ_{234} ε 25 400; CD (cyclohexane) $\Delta\epsilon_{245}$ +0.86, $\Delta\epsilon_{236}$ +1.78, $\Delta\epsilon_{225}$ +1.17, $\Delta\epsilon_{210}$ –1.42, and $\Delta\epsilon_{190}$ +4.58; MS (EI), *m/e* 190 (91, $M^{\cdot+}$), 175, 161, 147, 131, 117, 105, and 91 (100), (high resolution) calcd for $C_{13}H_{18}O$ 190.1358, found 190.1358.

(*E*)-(1*R*)-4(e)-[(Dimethyl-*tert*-butylsilyl)oxy]-2-adamantylideneacetaldehyde. By use of a previous procedure, silyl ether ester (0.18 g, 84% ee) was treated with AlH_3 (5 equiv) and on workup and purification yielded the alcohol as a solid (0.13 g, 79%): mp 53–55 °C; $[\alpha]^{26}_{Hg}$ +22.89 ± 0.1° (*c* 1.09, $CHCl_3$); IR ($CHCl_3$) 3580 (sharp), 3400 (broad), 2920, 2860, and 1670 cm^{-1}; ^1H NMR 0.03, 0.04 (2 s, 2 CH_3, 6 H), 0.91 (s, 9 H), 1.1 (br s, 1 H, OH), 1.4–2 (m, 8 H), 2.15–2.4 (m, 3 H), 2.78 (br s, 1 H), 3.74 (br s, 1 H), 4.11–4.15 (br dd, 4.13 doublet, *J* = 7 Hz, in D_2O exchange spectrum, 2 H), and 5.36 (t, *J* = 7 Hz, 1 H) ppm. Anal. Calcd for $C_{18}H_{32}O_2Si$: C, 70.13; H, 10.39. Found: C, 70.06; H, 10.4.

MnO_2 oxidation of the alcohol (0.12 g) for 1 h in 15 mL of hexane gave 0.1 g of silyl ether aldehyde as a solid: mp 80–84 °C; $[\alpha]^{26}_{Hg}$ +43.29 ± 0.1° (*c* 0.58, $CHCl_3$); IR ($CHCl_3$) 2925, 2860, 1670, and 1630 cm^{-1}; ^1H NMR 0.04 (s, 6 H), 0.91 (s, 9 H), 1.4–2.1 (m, 8 H), 2.26 (br d, *J* = 12.5 Hz, 1 H), 2.41 (br s, 2 H), 3.54 (br s, 1 H), 3.8 (br s, 1 H), 5.82 (d, *J* = 8 Hz, 1 H), and 9.99 (d, *J* = 8 Hz, 1 H) ppm; UV (cyclohexane) λ_{380} ε 21, λ_{362} ε 49, λ_{347} ε 63, λ_{333} ε 59, λ_{322} ε 47, λ_{310} ε 35, λ_{300} ε 27, and λ_{242} ε 18 750, (CH_3CN) λ_{366} ε 22, λ_{348} ε 55, λ_{334} ε 71, λ_{324} ε 70, λ_{310} ε 55, λ_{302} ε 44, and λ_{247} ε 19 000; CD (cyclohexane) $\Delta\epsilon_{399}$ –0.007, $\Delta\epsilon_{380}$ –0.046, $\Delta\epsilon_{362}$ –0.072, $\Delta\epsilon_{347}$ –0.066, $\Delta\epsilon_{334}$ –0.045, $\Delta\epsilon_{238}$ +4.21, and $\Delta\epsilon_{205}$ –1.45, (CH_3CN)

$\Delta\epsilon_{375}$ −0.0066, $\Delta\epsilon_{360}$ −0.003, $\Delta\epsilon_{348}$ +0.016, $\Delta\epsilon_{333}$ +0.033, $\Delta\epsilon_{322}$ +0.036, $\Delta\epsilon_{310}$ +0.027, $\Delta\epsilon_{302}$ +0.02, $\Delta\epsilon_{244}$ +4.32, and $\Delta\epsilon_{214}$ −1.87. Anal. Calcd for $C_{18}H_{30}O_2Si$: C, 70.59; H, 9.8. Found: C, 70.6; H, 9.8.

(*E*)-(1*R*)-4(e)-[(Dimethyl-*tert*-butylsilyl)oxy]-2-adamantylidenepropene. Via an earlier procedure, hydroxypropene (0.12 g 92% ee) was silylated. The crude mixture on workup and separation gave 12 mg of starting material and 150 mg (78%) of silyl ether propene as a liquid: $[\alpha]^{27}_{Hg}$ +31.12 ± 0.47° (*c* 0.28, cyclohexane); IR (film) 3060, 3020, 2900, 2840, 1800, 1650, and 1600 cm^{-1}; ^{1}H NMR 0.03 (s, 3 H), 0.04 (s, 3 H), 0.91 (s, 9 H), 1.4–2 (m, 8 H), 2.2–2.4 (m, 3 H), 2.93 (br s, 1 H), 3.75 (br t, J = 3.14 Hz, 1 H), 4.96 (m, 1.8, 2.5, 10 Hz, 1 H), 5.12 (m, J = 0.5, 1.8, 2.4, 17 Hz, 1 H), 5.79 (d, J = 10.97 Hz, 1 H), and 6.6 (sextet, J = 10.5, 10.6, 16.8 Hz, 1 H) ppm; UV (cyclohexane) λ_{250} ϵ 17 400, λ_{242} ϵ 26 900, and λ_{236} ϵ25 000; CD (cyclohexane) $\Delta\epsilon_{246}$ +1.34, $\Delta\epsilon_{235}$ +2.17, $\Delta\epsilon_{225}$ +1.66, $\Delta\epsilon_{205}$ −1.02, $\Delta\epsilon_{190}$ +0.64, (*c* unknown, CH_3CN) $\Delta\epsilon_{239^+}$, $\Delta\epsilon_{235^+}$, and $\Delta\epsilon_{203^-}$; MS (EI), *m/e* 304 ($M^{\bullet+}$), 289, 247 (100), 173, 131, 117, 91, and 75, (high resolution) calcd for $C_{19}H_{32}OSi$ 304.2222, found 304.2193.

(*E*)-(1*R*)-4(e)-Methoxy-2-adamantylidenepropene. A mixture of hydroxypropene (25 mg, 92% ee), NaH (50 mg), and CH_3I (0.5 mL) in 5 mL of dry THF was stirred at 25 °C for 16 h. Water was added, and the product was extracted with ether (3 × 10 mL). The combined ether extract was washed with water, dried (Na_2SO_4), and concentrated. The crude product on radial chromatography using hexane–ether (100:1) gave 24 mg of propene as a liquid: $[\alpha^{27}_{Hg}$ +40.9 ± 0.92° (*c* 0.24, cyclohexane); IR (CCl_4) 3065, 3025, 2900 (m), 1800 (w), and 1650 cm^{-1}; ^{1}H NMR 1.5–1.62 (m, 3 H), 1.65–1.86 (m, 3 H), 1.93 (td, J = 2.9, 12.6 Hz, 1 H), 2.07–2.3 (m, 3 H), 2.54 (br s, 1 H), 2.97 (br s, 1 H), 3.29 (br t, 1 H), 3.35 (s, 3 H), 4.97 (m, J = 0.7, 1.9, 2.6, 9.8 Hz, 1 H), 5.13 (m, J = 0.7, 1.9, 2.6, 17 Hz, 1 H), 5.82 (d, J = 10.9 Hz, 1 H), and 6.59 (sextet, J = 10.5, 10.6, 16.9 Hz, 1 H) ppm; UV (cyclohexane) λ_{250} ϵ 18 500, λ_{242} ϵ 28 800, and λ_{235} ϵ 26 600; CD (cyclohexane) $\Delta\epsilon_{247}$ +1.22, $\Delta\epsilon_{235}$ +2.41, $\Delta\epsilon_{210}$ −0.15, and $\Delta\epsilon_{198}$ +0.61; MS (EI), *m/e* 204 (100, $M^{\bullet+}$), 189, 174, 161, 143, 131, 117, and 91, (high resolution) calcd for $C_{14}H_{20}O$ 204.1514, found 204.1515.

(*Z*)-(1*R*)-4(a)-Hydroxy-2-adamantylideneacetone. A solution of hydroxy aldehyde (80 mg, 92% ee) in 5 mL of dry THF was added to MeMgCl (0.75 mL, 5 equiv, 2.8 M solution in THF) at 0 °C. The reaction mixture was stirred at 25 °C for 30 min and at refluxing temperature for 5 min and cooled to 0 °C. Aqueous NH_4Cl was added, and the mixture was extracted with ether (3 × 20 mL). The combined ether solution was washed with water, dried (Na_2SO_4), and concentrated to give 90 mg of mixture of the corresponding methyl glycols in the ratio of 56:44: ^{1}H NMR 1.26, 1.29 (2 d, J = 6.2, 6.6 Hz, 3 H), 1.5–2 (m, 11 H), 2.28 (br s, 1 H), 2.62 (br, 1 H, OH), 2.98 (br s, 1 H), 3.92, 3.99 (2 br s, 1 H), 4.49–4.65 (m, 1 H), and 5.41, 5.44 (2 d, J = 4.9, 5.5 Hz, 1 H) ppm.

The above crude methyl glycols in 20 mL of CH_2Cl_2 was treated with 2 g of active MnO_2 for 4 h. The product was filtered free of MnO_2 and concentrated to give a mixture of two compounds. Radial chromatography separation of the mixture using hexane–ether (5:1) gave 5 mg of (*Z*)-(1*R*)-4-oxo-2-adamantylideneacetone and polar hydroxy acetone (68 mg, 80%) as a white solid: mp 65–66 °C; $[\alpha]^{24}_{Hg}$ −212.07 ± 1.67° (*c* 0.21, cyclohexane), $[\alpha]^{24}_{Hg}$ −183.07 ± 0.7° (*c* 0.23, $CHCl_3$); IR (CCl_4) 3674, 3606 (free OH), 3471 (bonded OH), 2917, 2853, 1674, and 1615 cm^{-1}; ^{1}H NMR 1.5–2 (m, 10 H), 2.21 (s, 3 H), 2.33 (br s, 1 H), 2.4 (s, 1 H, OH), 3.97 (br s, 1 H), 4.09 (br s, 1 H), and 6.17 (s, 1 H) ppm; UV (cyclohexane) λ_{320} ϵ 94, and λ_{246} ϵ 11 000; CD (cyclohexane) $\Delta\epsilon_{325}$ −0.42, $\Delta\epsilon_{313}$ −0.39, $\Delta\epsilon_{249}$ −9.33, and $\Delta\epsilon_{204}$ +9.73; MS (EI), *m/e* 206 (100, $M^{\bullet+}$), 188, 178, 163, 145, 136, 135, 120, 105, and 91, (high resolution) calcd for $C_{13}H_{18}O_2$ 206.1307, found 206.1308.

(*Z*)-(1*R*)-4(e)-Hydroxy-2-adamantylideneacetone. To a stirred solution of hydroxy aldehyde (0.1 g, 92% ee) in THF was treated with MeMgCl to give after workup, 0.11 g of 2:1 (^{1}H NMR) mixture of methyl glycols: ^{1}H NMR 1.27, 1.28 (2 d, 3 H), 1.4–2 (m, 10 H), 2.1–2.3 (m, 3 H), 2.85 (br s, 1 H), 3.75, 3.82 (2 s, 1 H), 4.55–4.7 (m, 1 H), and 5.23 (d, 1 H).

The above methyl glycol in 20 mL of CH_2Cl_2 was oxidized with active MnO_2 for 6 h to give 4 mg of less polar (*Z*)-(1*R*)-4-oxo-2-adamantylideneacetone and polar hydroxy acetone (80 mg, 82%): $[\alpha]^{26}_{Hg}$ +16.6 ± 1.4° (*c* 0.1, $CHCl_3$); IR (CCl_4) 3614 (free OH), 3445 (bonded OH), 2920, 2860, 1685, and 1610 cm^{-1}; ^{1}H NMR 1.5–2.4 (m, 12 H), 2.18 (s, 3 H), 3.84 (br t, 1 H),4.07 (br s, 1 H), and 6.02 (s, 1 H) ppm; UV (cyclohexane) λ_{322} ϵ 64, and λ_{244} ϵ 9300; CD (cyclohexane) $\Delta\epsilon_{352}$ −0.018, $\Delta\epsilon_{315}$ +0.078, $\Delta\epsilon_{303}$ +0.128, $\Delta\epsilon_{295}$ +0.122, $\Delta\epsilon_{246}$ −1.33, and $\Delta\epsilon_{215}$ +4.25; MS (EI), *m/e* 206 (100, $M^{\bullet+}$), 188, 178, 163, 145, 136, 135, 121, 105, and 91, (high resolution) calcd for $C_{13}H_{18}O_2$ 206.1307, found 206.1308.

(*E*)-(1*R*)-4(a)-Hydroxy-2-adamantylideneacetone. The hydroxy aldehyde (0.1 g, 92% ee) in THF was treated with MeMgCl as earlier to give a mixture of the corresponding methyl glycols. MnO_2 oxidation of the crude methyl glycols in CH_2Cl_2 for 6 h gave after purification 10 mg of less polar (*E*)-(1R)-4-oxo-2-adamantylideneacetone and polar hydroxy acetone (80 mg, 74%): $[\alpha]^{24}_{Hg}$ +38.52 ± 0.82° (*c* 0.19, cyclohexane); IR (CCl_4) 3673 (free OH), 3608 (free OH), 3464 (bonded OH), 2914, 2854, 1682, and 1614 cm^{-1}; ^{1}H NMR 1.5–2.15 (m, 11 H), 2.19 (s, 3 H), 2.38 (br s, 1 H), 4.01 (br s, 2 H), and 6.03 (s, 1 H) ppm; UV (cyclohexane) λ_{330} ϵ 57, λ_{312} ϵ 50, and λ_{242} ϵ 12 000; CD (cyclohexane) $\Delta\epsilon_{330}$ +0.04, $\Delta\epsilon_{315}$ +0.11, $\Delta\epsilon_{304}$ +0.14, $\Delta\epsilon_{295}$ +0.13, $\Delta\epsilon_{240}$ +3.14, and $\Delta\epsilon_{210}$ −3.92; MS (EI), *m/e* 206 (100, $M^{\bullet+}$), 188, 178, 163, 145, 136, 135, 121, 105, and 91, (high resolution) calcd for $C_{13}H_{18}O_2$ 206.1307, found 206.1308.

(*E*)-(1*R*)-4(e)-Hydroxy-2-adamantylideneacetone. Via an earlier procedure, 120 mg of hydroxy aldehyde (92% ee) was treated with MeMgCl in THF to give the corresponding 1:1 mixture of diastereomeric methyl glycols: ^{1}H NMR 1.23, 1.25 (2 d, J = 5.8, 6.2 Hz, 3 H), 1.3–2 (m, 10 H), 2.1–2.3 (m, 2 H), 2.33 (br s, 1 H), 2.8 (br s, 1 H), 3.8, 3.85 (2 br t, 1 H), 4.6 (m, 1 H) and 5.21 (d, J = 8 Hz, 1 H) ppm. The crude methylglycols in CH_2Cl_2 were oxidized with MnO_2 to produce after purification 14 mg of less polar (*E*)-(1*R*)-4-oxo-2-adamantylideneacetone and polar hydroxy acetone (100 mg, 80%): $[\alpha]^{25}_{Hg}$ +43.88 ± 0.1° (*c* 0.25, cyclohexane); IR (CCl_4) 3615 (free OH), 3485 (bonded OH), 2920, 2854, 1683, and 1611 cm^{-1}; ^{1}H NMR 1.2–2 (m, 10 H), 2.18 (s, 3 H), 2.3–2.45 (m, 2 H), 3.85 (br s, 1 H), 4 (br s, 1 H), and 6.01 (s, 1 H) ppm; UV (cyclohexane) λ_{330} ϵ 62, and λ_{243} ϵ 12 800; CD (cyclohexane) $\Delta\epsilon_{340}$ −0.059, $\Delta\epsilon_{290}$ +0.14, $\Delta\epsilon_{240}$ +1.73, and $\Delta\epsilon_{202}$ +1.63; MS (EI), *m/e* 206 (100, $M^{\bullet+}$), 188, 178, 163, 145, 136, 135, 117, 105, and 91, (high resolution) calcd for $C_{13}H_{18}O_2$ 206.1307, found 206.1308.

Methyl (*Z*)-(1*R*)-4(e)-Hydroxy-4(a)-methyl- and Methyl (*Z*)-(1*R*)-4(a)-Hydroxy-4(e)-methyl-2-adamantylideneacetates. To a stirred solution of (*Z*)-(1*R*)-4-oxo ester 1.8 g, 92% ee) in 20 mL of dry THF was added 4.34 mL (1.5 equiv) of CH_3MgCl (2.8 M solution in THF) at −78 °C. The reaction mixture was allowed to come to room temperature. After 20 h, workup and separation gave three fractions. The less polar fraction yielded a semisolid (1.72 g, 90%), identified as (*Z*)-(1*R*)-4(e)-hydroxy-4(a)-methyl ester: mp 60–68 °C; $[\alpha]^{26}_{Hg}$ −7.5 ± 0.63° (*c* 0.26, cyclohexane); IR (CCl_4) 3580 (sharp), 3460 (broad), 2900 (m), 1715, and 1645 cm^{-1}; ^{1}H NMR 1.24 (s, 3 H), 1.5–1.7 (m, 3 H), 1.75–2 (m, 6 H, including OH), 2.25–2.5 (m, 3 H), 3.69 (s, 3 H), 3.93 (br s, 1 H), and 5.67 (s, 1 H) ppm: ^{13}C NMR see Table VII; UV (cyclohexane) λ_{228} ϵ 14 260; CD (cyclohexane) $\Delta\epsilon_{228}$ −5.5, and $\Delta\epsilon_{190}$ +7.62. Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.18; H, 8.47. Found: C, 71.17; H, 8.44.

The polar second fraction gave traces of impure (*Z*)-(1*R*)-4-(a)-hydroxy-4(e)-methyl ester; ^{1}H NMR 1.39 (s, 3 H, CH_3), 1.5–2.5 (m, 12 H), 3.69 (s, 3 H), 3.96 (br s, 1 H), and 6.04 (s, 1 H) ppm.

The last fraction (15 mg) had no ester group and it was not analyzed.

Methyl (*Z*)-(1*R*)-4-Methylene-2-adamantylideneacetate. A mixture of 1.7 g of (*Z*)-(1*R*)-4(e)-hydroxy-4(a)-methyl ester and 70 mg of *p*-toluenesulfonic acid in 150 mL of benzene was refluxed with azeotropic removal of water for 6 h. The reaction mixture was cooled and filtered through silica gel (100 g) with hexane–ether (1:1). The combined solvents were concentrated. The crude product on chromatography purification yielded 1.33 g (85%) of less polar fraction and 0.02 g of polar components. The less polar fraction, a colorless liquid, was found to be the required methylene ester: $[\alpha]^{24}_{Hg}$ −104.38 ± 0.76° (*c* 0.26, cyclohexane); IR (CCl_4) 3055 (w), 2965, 2900, 2840, 1715, and 1650 cm^{-1}; ^{1}H NMR 1.6–2.1 (m, 10 H), 2.49 (br s, 1 H), 2.56 (br s, 1 H), 3.69 (s, 3 H), 4.58 (d, J = 1.9 Hz, 1 H), 4.7 (1 br s, 1 d, J = 1.8 Hz, 2 H), and 5.56 (s, 1 H) ppm; UV (cyclohexane) λ_{224} ϵ 16 400; CD (cyclohexane) $\Delta\epsilon_{230}$ −7, and $\Delta\epsilon_{193}$ +13.89. Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.06; H, 8.25. Found: C, 77.1; H, 8.2.

Methyl (*Z*)-(1*R*)-4(a)- and -4(e)-Methyl-2-adamantylideneacetates. By use of the Wilkinson catalyst,[9] chlorotris(triphenylphosphine)rhodium(I), the required 4(a)- and 4(e)-methyl isomers were prepared. Accordingly, to a solution of methylene ester (1 g) in 75 mL of benzene was added $(Ph_3P)_3RhCl$ (0.8 g) and stirred under a hydrogen atmosphere for 2 days. A small portion was analyzed by ^1H NMR spectroscopy. Once the reaction was complete, the reaction mixture was filtered through 200 g of silica gel with CH_2Cl_2 and concentrated. The crude reaction mixture on radical chromatography purification with 20:1 hexane–ether gave 1 g of the mixture of the (*Z*)-(1*R*)-4(a) and (*Z*)-(1*R*)-4(e) esters in 2:1 ratio, respectively (^1H NMR). All the attempts to separate these two isomers were unsuccessful. Only a partial separation was achieved. The less polar isomer had the following ^1H NMR spectrum corresponding to the (*Z*)-(1*R*)-4(a)-methyl ester: 0.92 (d, J = 7.3 Hz, 3 H), 1.4–2.2 (m, 11 H), 2.34 (br s, 1 H), 3.67 (s, 3 H), 3.86 (br s, 1 H), and 5.7 (s, 1 H) ppm. The polar isomer, (*Z*)-(1*R*)-4(e)-methyl ester exhibited the following ^1H NMR signals at 1.13 (d, J = 7.3 Hz, 3 H), 1.4–2.2 (m, 11 H), 2.41 (br s, 1 H), 3.6 (s, 3 H), 3.78, (br s, 1 H), and 5.56 (s, 1 H) ppm.

(*Z*)-(1*R*)-4(a)- and -4(e)-Methyl-2-adamantylideneethanols. To a stirred slurry of AlH_3 was added 1 g of above mixture of 4(a)-methyl and 4(e)-methyl esters at 0 °C. After 30 min the reaction was worked up as earlier. The mixture of alcohols (0.8 g) was subjected to repeated radial chromatography with 20:1 hexane–ether. The fractions corresponding to the pure isomers (^1H NMR) were collected. The less polar isomer (230 mg) identified as 4(a)-methyl alcohol, a colorless liquid: IR (film) 3300 (broad), 2900, 2840, and 1665 cm^{-1}; ^1H NMR 0.9 (d, J = 7 Hz, 3 H), 1.2 (br s, 1 H, OH), 1.5–2 (m, 11 H), 2.28 (br s, 1 H), 2.59 (br s, 1 H), 4.1 (dd, J = 1.5, 7 Hz, 2 H), and 5.48 (t, J = 7 Hz, 1 H) ppm. Anal. Calcd for $C_{13}H_{20}O$: C, 81.25; H, 10.41. Found: C, 80.96; H, 10.41.

Polar fraction (0.18 g) gave impure 4(e)-methyl alcohol: ^1H NMR 1.1 (d, J = 7 Hz, 3 H), 1.41–2.12 (m, 12 H), 2.35 (br s, 1 H), 2.56 (br s, 1 H), 4.12 (d, J = 7 Hz, 2 H), and 5.32 (t, J = 7 Hz, 1 H) ppm.

(*Z*)-(1*R*)-4(a)-Methyl-2-adamantylideneacetaldehyde. (4a)-Methyl alcohol (0.2 g) in 25 mL of hexane was oxidized with active MnO_2 (2 g) for 2 h. MnO_2 was filtered off, and the solvent was concentrated. The product on radial chromatography purification using hexane–ether (20:1) yielded 0.18 g (89%) of pure 4(a)-methyl aldehyde: $[\alpha]^{25}_{Hg}$ −15.01 ± 0.09° (*c* 0.3, cyclohexane); IR (CCl_4) 2900, 2840, 2740 (w), 1675, 1630, and 1610 cm^{-1}; ^1H NMR 0.95 (d, J = 7 Hz, 3 H), 1.5–2.2 (m, 11 H), 2.45 (br s, 1 H), 3.37 (br s, 1 H), 5.95 (d, J = 8 Hz, 1 H), and 9.98 (d, J = 8 Hz, 1 H) ppm; UV (cyclohexane) λ_{400} ε 2, λ_{379} ε 24, λ_{361} ε 58, λ_{345} ε 75, λ_{331} ε 70, λ_{318} ε 61, λ_{296} ε 89, λ_{287} ε 95, λ_{241} ε 19 600, and λ_{237} ε 19 800; CD (cyclohexane) $\Delta\epsilon_{399}$ −0.006, $\Delta\epsilon_{384}$ −0.009, $\Delta\epsilon_{377}$ −0.015, $\Delta\epsilon_{368}$ −0.024, $\Delta\epsilon_{358}$ −0.025, $\Delta\epsilon_{352}$ −0.038, $\Delta\epsilon_{337}$ −0.04, $\Delta\epsilon_{325}$ −0.03, $\Delta\epsilon_{314}$ −0.018, $\Delta\epsilon_{303}$ −0.009, $\Delta\epsilon_{292}$ −0.0037, $\Delta\epsilon_{236}$ +0.83, and $\Delta\epsilon_{206}$ −2.41.

(*Z*)-(1*R*)-4(a)-Methyl-2-adamantylidenepropene. Following an earlier procedure, 0.1 g of 4(a)-methyl aldehyde was condensed with methylenetriphenylphosphorane. The crude product on radial chromatography (two times) using hexane yielded 79 mg (80%) of pure colorless liquid corresponding to methyl propene: $[\alpha]^{25}_{Hg}$ +4.86 ± 0.88° (*c* 0.17, cyclohexane); IR (CCl_4) 3075, 3017, 2900, 2820, 1990 (w), 1650, and 1600 (w) cm^{-1}; ^1H NMR 0.89 (d, J = 6.9 Hz, 3 H), 1.5–2.1 (m, 11 H), 2.28 (br s, 1 H), 2.78 (br s, 1 H), 4.92 (dd, J = 2.3, 9.9 Hz, 1 H), 5.09 (dd, J = 2.3, 16.8 Hz, 1 H), 5.91 (d, J = 10.9 Hz, 1 H), and 6.58 (m, J = 10.5, 10.6, 16.7 Hz, 1 H) ppm; UV (cyclohexane) λ_{249} ε 18 900, λ_{240} ε 29 300, and λ_{233} ε 27 200; CD (cyclohexane) $\Delta\epsilon_{247}$ +0.93, $\Delta\epsilon_{240}$ +1.46, $\Delta\epsilon_{234}$ +1.86, and $\Delta\epsilon_{198}$ −0.79. Anal. Calcd for $C_{14}H_{20}$: C, 89.36; H, 10.64. Found: C, 89.27; H, 10.68.

(*Z*)-(1*R*)-4(a)-Methyl-2-adamantylideneacetone. To a cooled solution of aldehyde (75 mg) in THF was added MeMgCl. The reaction mixture after workup gave 80 mg of methyl carbinols (3:1 ratio, ^1H NMR), which was further treated with active MnO_2 in hexane for 3 h. The product was filtered and on usual purification gave 54 mg (80%) of 4-methyl acetone as a liquid: $[\alpha]^{25}_{Hg}$ −69.96 ± 0.28° (*c* 0.21, cyclohexane); IR (CCl_4) 2950, 2900, 2840, 1686, and 1615 cm^{-1}; ^1H NMR 0.90 (d, J = 7 Hz, 3 H), 1.5–2.1 (m, 11 H), 2.17 (s, 3 H), 2.25 (br s, 1 H), 3.86 (br s, 1 H), and 6.08 (s, 1 H) ppm; UV (cyclohexane) λ_{330} ε 74, and λ_{243} ε 14 800; CD (cyclohexane) $\Delta\epsilon_{336}$ −0.22, $\Delta\epsilon_{247}$ −1.36, and $\Delta\epsilon_{204}$ −0.59. Anal. Calcd for $C_{14}H_{20}O$: C, 82.35; H, 9.8. Found: C, 82.34; H, 9.83.

(*Z*)-(1*R*)-4(e)-Methyl-2-adamantylideneacetaldehyde. A mixture of 0.1 g of methyl alcohol and 1 g of active MnO_2 in hexane was stirred for 3 h. After the usual workup and purification there was isolated 90 mg (91%) of aldehyde as a liquid: $[\alpha]^{25}_{Hg}$ +36.34 ± 0.95° (*c* 0.2, cyclohexane); IR (CCl_4) 2950, 2900, 2840, 2750 (w), 1665, 1630, and 1610 (w) cm^{-1}; ^1H NMR 1.17 (d, J = 7 Hz, 3 H), 1.5–2.15 (m, 10 H), 2.23 (d q, 1 H, J = 2.7, 12.98 Hz, 1 H), 2.52 (br s, 1 H), 3.31 (br s, 1 H), 5.8 (d, J = 8.3 Hz, 1 H), and 10.01 (d, J = 8.3 Hz, 1 H) ppm; UV (cyclohexane) λ_{400} ε 1, λ_{379} ε 23, λ_{361} ε 53, λ_{345} ε 66, λ_{332} ε 59, λ_{320} ε 44, λ_{310} ε 30, λ_{300} ε 18, λ_{242} ε 19 000, and λ_{237} ε 19 400; CD (cyclohexane) $\Delta\epsilon_{400}$ −0.002, $\Delta\epsilon_{378}$ −0.08, $\Delta\epsilon_{360}$ −0.167, $\Delta\epsilon_{346}$ −0.162, $\Delta\epsilon_{331}$ −0.11, $\Delta\epsilon_{320}$ −0.056, $\Delta\epsilon_{309}$ −0.024, $\Delta\epsilon_{300}$ −0.008, $\Delta\epsilon_{236}$ +1.71, $\Delta\epsilon_{208}$ −0.74, and $\Delta\epsilon_{194}$ +1.6. Anal. Calcd for $C_{13}H_{18}O$: C, 82.1; H, 9.47. Found: C, 82.19; H, 9.6.

(*Z*)-(1*R*)-4(e)-Methyl-2-adamantylidenepropene. By use of an earlier procedure, 80 mg of methyl aldehyde was condensed with methylenetriphenylphosphorane. Workup and purification of crude product gave 47 mg (59%) of methylpropene as a colorless liquid: $[\alpha]^{25}_{Hg}$ +54.09 ± 0.6° (*c* 0.15, cyclohexane); IR (CCl_4) 3070, 3015, 2970, 2800, 2740, 1790 (w), and 1647 cm^{-1}; ^1H NMR 1.1 (d, J = 7 Hz, 3 H), 1.4–2.1 (m, 11 H), 2.36 (br s, 1 H), 2.71 (br s, 1 H), 4.92 (dd, J = 1.99, 10.2 Hz, 1 H), 5.09 (dd, J = 1.99, 16.7 Hz, 1 H), 5.75 (d, J = 10.9 Hz, 1 H), and 6.62 (m, J = 10.5, 10.6, 16.7 Hz, 1 H) ppm; UV (cyclohexane) λ_{249} ε 19 400, λ_{241} ε 29 700, and λ_{234} ε 27 500; CD (cyclohexane) $\Delta\epsilon_{249}$ +0.91, $\Delta\epsilon_{238}$ +1.14, and $\Delta\epsilon_{206}$ +2.43. Anal. Calcd for $C_{14}H_{20}$: C, 89.36; H, 10.64. Found: C, 89.42; H, 10.84.

Methyl (*E*)-(1*R*)-4(e)-Hydroxy-4(a)-methyl- and Methyl (*E*)-(1*R*)-4(a)-Hydroxy-4(e)-methyl-2-adamantylideneacetates. Via an earlier procedure, methyl (*E*)-(1*R*)-4-oxo-2-adamantylideneacetate, (1.33 g, 92% ee) was treated with CH_3-MgCl (3.22 mL, 1.5 equiv, 2.8 M solution in THF) in dry THF at −78 °C. Workup and chromatography separation gave three fractions. The less polar fraction solidified on standing to give (*E*)-(1*R*)-4(e)-hydroxy-4(a)-methyl ester (1.25 g, 88%): mp 78–79 °C; $[\alpha]^{26}_{Hg}$ +36.55 ± 0.35° (*c* 0.27, cyclohexane); IR (CCl_4) 3580 (sharp), 3380 (broad), 2900 (m), 1715, and 1645 cm^{-1}; ^1H NMR 1.2 (s, 3 H), 1.63, (br d, J = 12.8 Hz, 2 H), 1.7–1.95 (m, 6 H), 1.98 (br s, 1 H, OH), 2.23 (br s, 1 H), 2.3 (br d, J = 1.9, 12.8 Hz, 1 H), 2.42 (dm, J = 2.7, 12.6 Hz, 1 H), 3.68 (s, 3 H), 4.01 (br s, 1 H), and 5.62 (s, 1 H) ppm; ^{13}C NMR see Table VII; UV (cyclohexane) λ_{228} ε 15 700; CD (cyclohexane) $\Delta\epsilon_{230}$ +1.03, and $\Delta\epsilon_{200}$ −2.27. Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.18; H, 8.47. Found: C, 71.22; H, 8.54.

Polar fraction gave 20 mg of impure (*E*)-(1*R*)-4(a)-hydroxy-4-(e)-methyl ester: ^1H NMR 1.38 (s, 3 H), 1.6–2.2 (m, 11 H), 2.23 (br s, 1 H), 3.68 (s, 3 H), 4.01 (br s, 1 H), and 5.67 (s, 1 H) ppm. The last fraction (15 mg) was not identified.

Methyl (*E*)-(1*R*)-4-Methylene-2-adamantylideneacetate. (*E*)-(1*R*)-4(e)-Hydroxy-4(a)-methyl ester, (1.2 g) and *p*-toluenesulfonic acid (50 mg) in benzene (120 mL) was refluxed with azeotropic removal of water for 6 h. Workup and purification gave 1.03 g (93%) of less polar fraction and 15 mg of polar fraction. The less polar fraction with the following spectral data was identified as the required 4-methylene ester, a colorless liquid: $[\alpha]^{24}_{Hg}$ +55.3 ± 0.08° (*c* 0.24, cyclohexane); IR (CCl_4) 3050, 2970, 2900, 2840, 1715, and 1650 cm^{-1}; ^1H NMR 1.7–2.1 (m, 9 H), 2.57 (br s, 1 H), 2.99 (br s, 1 H), 3.67 (s, 3 H), 4.13 (br s, 1 H), 4.56 (s, 2 H), and 5.59 (s, 1 H) ppm; UV (cyclohexane) λ_{224} ε 17 100; CD (cyclohexane) $\Delta\epsilon_{265}$ −1.94, and $\Delta\epsilon_{225}$ +10.92. Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.06; H, 8.25. Found: C, 77.1; H, 8.2.

Methyl (*E*)-(1*R*)-4(a)- and -4(e)-Methyl-2-adamantylideneacetates. A solution of 0.74 g of 4-methylene ester and 0.5 g of $(Ph_3P)_3RhCl$ in 75 mL of benzene was stirred under H_2 atmosphere. When all the starting material had disappeared (^1H NMR), the benzene solution was filtered through 150 g of silica gel. The crude product was purified to give in quantitative yield of the title compounds a-CH_3 and e-CH_3 esters in the ratio of 6:4, respectively (^1H NMR). Separation of the methyl esters was tried with different solvent mixtures; only a partial separation was achieved. The less polar isomer showed the following ^1H NMR signals at 0.9 (d, 3 H), 3.68 (s, 3 H), 3.97 (br s, 1 H), and 5.55 (s, 1 H) ppm, while the polar compound had the main ^1H NMR signals at 1.1 (d, 3 H), 3.68 (s, 3 H), 4.05 (br s, 1 H), and 5.57 (s, 1 H) ppm.

(*E*)-(1*R*)-4(a)- and -4(e)-Methyl-2-adamantylideneacetaldehydes. AlH_3 reduction of the above mixture (0.7 g) gave the corresponding 4(a)- and 4(e)-methyl alcohols. The mixture of the alcohols (0.66 g) could not be separated into two pure isomers, and the separation was tried in the next step.

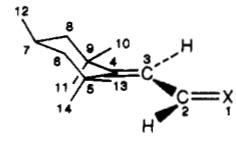
The mixture of alcohols on oxidation with MnO_2 as earlier gave the corresponding aldehydes. The mixture (0.6 g) on repeated radial chromatography separation with 20:1 hexane–ether gave the two pure isomers. However, during separation most of the product was decomposed. The less polar fraction solidified on standing to give 60 mg of 4(a)-methyl aldehyde: mp 50–54 °C; $[\alpha]^{21}_{Hg}$ +3.49 ± 0.1° (*c* 0.26, cyclohexane); IR (CCl_4) 2917, 2852, 2750 (w), 1670, 1626, and 1608 (w) cm^{-1}; ^1H NMR 0.92 (d, *J* = 7 Hz, 3 H), 1.7–2.2 (m, 11 H), 2.27 (br s, 1 H), 3.54 (br s, 1 H), 5.8 (d, *J* = 8.3 Hz, 1 H), and 10 (d, *J* = 8.4 Hz, 1 H) ppm; UV (cyclohexane) λ_{400} ε 1, λ_{380} ε 22, λ_{362} ε 53, λ_{346} ε 66, λ_{333} ε 59, λ_{322} ε 45, λ_{310} ε 29, λ_{300} ε 18, λ_{243} ε 18900, λ_{239} ε 19000; CD (cyclohexane) $\Delta\epsilon_{380}$ −0.06, $\Delta\epsilon_{362}$ −0.15, $\Delta\epsilon_{347}$ −0.18, $\Delta\epsilon_{332}$ −0.14, $\Delta\epsilon_{320}$ −0.09, $\Delta\epsilon_{310}$ −0.05, $\Delta\epsilon_{300}$ −0.02, $\Delta\epsilon_{238}$ +1.95, and $\Delta\epsilon_{208}$ −2.57.

The polar fraction gave 26 mg of 4(e)-methyl aldehyde as a liquid: $[\alpha]^{25}_{Hg}$ +53.45 ± 0.8° (*c* 0.23, cyclohexane); IR (CCl_4), 2900, 2850, 2740, 1675, 1630, and 1610 (w) cm^{-1}; ^1H NMR 1.13 (d, *J* = 7 Hz, 3 H), 1.63 (br d, *J* = 12.2 Hz, 2 H), 1.7–2.17 (m, 9 H), 2.25 (br s, 1 H), 3.61 (br s, 1 H), 5.8 (d, *J* = 8.4 Hz, 1 H), and 10.3 (d, 8.3 Hz, 1 H) ppm; UV (cyclohexane) λ_{400} ε 1, λ_{379} ε 21, λ_{361} ε 48, λ_{345} ε 61, λ_{332} ε 55, λ_{320} ε 43, λ_{310} ε 31, λ_{300} ε 23, λ_{242} ε 17600, and λ_{238} ε 17800; CD (cyclohexane) $\Delta\epsilon_{379}$ +0.05, $\Delta\epsilon_{360}$ +0.12, $\Delta\epsilon_{345}$ +0.14, $\Delta\epsilon_{331}$ +0.11, $\Delta\epsilon_{319}$ +0.05, $\Delta\epsilon_{300}$ −0.03, $\Delta\epsilon_{290}$ −0.04, $\Delta\epsilon_{280}$ −0.02, $\Delta\epsilon_{238}$ +2.47, and $\Delta\epsilon_{208}$ −1.38.

(*E*)-(1*R*)-4(a)-Methyl-2-adamantylidenepropene. Via an earlier procedure, methylenetriphenylphosphorane was condensed with 60 mg of methyl aldehyde. The product was isolated and purified to obtain 7 mg of methyl propene as a liquid: $[\alpha]^{19}_{Hg}$ +14.61 ± 0.2° (*c* 0.13, cyclohexane); IR (CCl_4) 3070, 3012, 2900, 2840, 1790, 1645, and 1600 (w) cm^{-1}; ^1H NMR 0.89 (d, *J* = 7 Hz, 3 H), 1.6–2 (m, 11 H), 2.07 (br s, 1 H), 2.92 (br s, 1 H), 4.92 (dd, *J* = 2.3, 10.2 Hz, 1 H), 5.09 (dd, *J* = 2.3, 16.8 Hz, 1 H), 5.74 (d, *J* = 11 Hz, 1 H), and 6.62 (m, *J* = 10.5, 10.6, 16.9 Hz, 1 H) ppm; UV (cyclohexane) λ_{249} ε 18200, λ_{241} ε 27500 and λ_{234} ε 25500; CD (cyclohexane) $\Delta\epsilon_{249}$ +0.92; $\Delta\epsilon_{240}$ +1.51, $\Delta\epsilon_{232}$ +1.68, and $\Delta\epsilon_{194}$ −2.1; MS (EI), *m/e* 188 (100, $M^{+\cdot}$), 173, 159, 145, 131, 117, 105, and 91, high resolution) calcd for $C_{14}H_{20}$ 188.1565, found 188.1565.

(*E*)-(1*R*)-4(e)-Methyl-2-adamantylidenepropene. Methylenetriphenylphosphorane was condensed with methyl aldehyde (20 mg) to give after workup and purification as earlier, 9 mg (45%) of methyl propene as a liquid: $[\alpha]^{20}_{Hg}$ +52.19 ± 0.17° (*c* 0.16, cyclohexane); IR (CCl_4) 3067, 3014, 2900, 2840, 1790, and 1650 cm^{-1}; ^1H NMR 1.07 (d, *J* = 7 Hz, 3 H), 1.5–2.2 (m, 12 H), 3.01 (br s, 1 H), 4.93 (dd, *J* = 2.3, 10.2 Hz, 1 H), 5.09 (dd, *J* = 2.2, 16.9 Hz, 1 H), 5.76 (d, *J* = 10.9 Hz, 1 H), and 6.62 (m, *J* = 10.3, 10.6, 16.9 Hz, 1 H) ppm; UV (cyclohexane) λ_{249} ε 18800, λ_{241} ε 28700, and λ_{235} ε 26800; CD (cyclohexane) $\Delta\epsilon_{248}$ +1.41, $\Delta\epsilon_{240}$ +2.42, $\Delta\epsilon_{232}$ +1.81, $\Delta\epsilon_{225}$ +1.34, $\Delta\epsilon_{210}$ −0.54, and $\Delta\epsilon_{190}$ +1; MS (EI), *m/e* 188 (100, $M^{+\cdot}$), 173, 159, 145, 131, 117, 105, 91 and 79, (high resolution) calcd for $C_{14}H_{20}$ 188.1565, found 188.1565.

MMP2 Calculations[21]



dihedral angle	X = CH_2	X = O
$C_1-C_2-C_3-C_4$	−176.68°	−169.86°
$C_2-C_3-C_4-C_5$	− 0.25°	0.85°
$C_2-C_3-C_4-C_9$	−171.46°	−171.02°
$C_3-C_4-C_5-C_{13}$	52.90°	50.27°
$C_3-C_4-C_5-C_{14}$	− 69.14°	− 72.29°
$C_3-C_4-C_9-C_{10}$	− 47.91°	− 45.16°
$C_3-C_4-C_9-C_{11}$	70.83°	73.31°
energy of conformer, kcal/mol	23.43	27.13

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(21) These calculations were made by Dr. M. Duraisamy using the facilities kindly provided by Professor N. L. Allinger at the University of Georgia.

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Syntheses and Chiroptical Properties of 4-Oxo- and 4-Methylene-2-adamantylidene Derivatives[1]

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The (*Z*)- and (*E*)-(1*R*)-4-oxo- and -4-methylene-2-adamantylidene derivatives of methyl acetate, acetone, acetaldehyde, 2-ethanol, and propene have been synthesized. Their *Z* and *E* configurations have been assigned by their ^1H and ^{13}C NMR spectra. All 4-oxo compounds obey the octant rule for their n–π* absorption. The Cotton effect for the π–π* absorption of the 4-methylene derivatives are of the same sign as for the 4-oxo compounds.

It had been observed that when a substituent is located in an equatorial position β to the carbonyl chromophore that the Octant rule is obeyed. However, if the substituent is axially located then the Octant rule is not followed.[2] To account for this anomaly it was originally suggested that the axial substituent belonged in a back octant[3] and later it was considered as an "antioctant" configuration.[4] Recently, Lightner, and co-workers[4,5] have provided convincing evidence that the axial substituent projects into

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