J. Am. Chem. Soc. **1988**, *110*, 4593–4599

configuration at C_β is not found at the syn TS. Probably, the minimum energy path sought by Bach et al.[18] deviates significantly from the true reaction coordinate.

Solvent Effect on E2 and S_N2. In the condensed phase, the β-hydrogen atom (acidic, shown in Figure 3) and the nucleophile X^- are surrounded by solvent molecules. Therefore, in the protic solvent, the first cluster is not formed, and the base strength is weakened considerably. The double desolvation (at the β proton and X^-) is required to arrive at the E2 TS, whereas the single desolvation (at X^-) is needed for S_N2. Thus, S_N2 proceeds more readily than E2 in the polar solvent. The most reactive site, H_β, in the gas phase is the most strongly solvated site to block the X^- attack.

Although the energy profile in the gas phase in Figures 1 and 2 is entirely different from that in the condensed phase, TS geometries are common to both phases. The solvation strength is essentially electrostatic, which cannot alter the geometric configuration. The invariance of the geometry with and without solvent molecules has been found in several studies. Bertrãn et al. searched for the first-cluster and TS geometries of S_N2 reactions: $F^- + CH_3F \rightarrow FCH_3 + F^-$ (gas phase) and $(H_2O)F^- + CH_3F(H_2O) \rightarrow (H_2O)FCH_3 + F^-(H_2O)$.[19] At the first cluster, the F···C distances are 2.31 and 2.33 Å without and with two water molecules, respectively. At TS, they are 1.78 and 1.79 Å. The invariance of the distance without and with solvent (water) molecules is surprising in view of the large $F^-\cdots H_2O$ binding energy (=23.3 kcal/mol, experimental).[13b] This result demonstrates that the solvation strength is mainly electrostatic.

In addition, recent theoretical studies have shown that the activation energies in the gas phase and aqueous media may be qualitatively reproduced in an S_N2 reaction: $Cl^- + CH_3Cl \rightarrow ClCH_3 + Cl^-$.[20] The solvation by over 200 water molecules is taken into account in the Monte Carlo simulation. Each water molecule is represented by four point charges ("TIP4P model"). The model prohibits the $Cl^- \rightarrow H_2O$ charge transfer and other (exchange and polarization) interactions. The validity of the model of the hydrated S_N2 reaction indicates again that the solvation may be described well as the Coulombic stabilization. In view of these results, our TS geometries may be applicable to the condensed-media reactions.

Concluding Remarks

The determination of the TS structures of three E2 and S_N2 reactions gives some information. All the eliminations are concerted and belong to the E2H category of Bunnett's variable TS spectrum. The elimination of EtCl by F^- has an early TS, while that of EtCl by Cl^- is late. The E2 TS is completely different from the S_N2 TS in three reactions adopted here, because the incipient π-electronic cloud expels an attacking base from the C_α–C_β region in the E2 TS.

The geometry of the syn E2 TS is similar to that of the anti TS. But, the syn – anti activation energy difference is larger than the conformational energy gap of eclipsed and staggered substrates. The extent of the intramolecular CT is the source of the former difference.

Acknowledgment. We thank the Institute for Molecular Science for the allotment of the CPU time of the HITAC M-680H computer.

Registry No. EtF, 353-36-6; EtCl, 75-00-3; F^-, 16984-48-8; Cl^-, 16887-00-6.

Supplementary Material Available: Tables of Cartesian coordinates and vibrational frequencies (16 pages). Ordering information is given on any current masthead page.

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Chiroptical Properties of Chiral Olefins[1]

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Abstract: A series of chiral (4-methylcyclohexylidene)(X,Y-substituted)methane derivatives have been prepared (i.e. X = CH_3, H, D and Y = Cl, Br, F). Their CD spectra in the vacuum ultraviolet have been recorded and discussed.

The optical activity of the olefin chromophore has been the subject of extensive theoretical[3–6] and experimental[7–15] investigation. The most comprehensive study of chiral olefins was undertaken by Drake and Mason.[3] They successfully assigned the first transition of the olefinic chromophore as the $\pi \rightarrow 3s$ Rydberg by dissolving the chiral olefin in a variety of solvents whereby the $\pi \rightarrow 3s$ broadened appreciably and was shifted to higher frequencies. When the solution was cooled, the Rydberg excitation continued to shift to higher energies. A different behavior was observed for the $\pi \rightarrow \pi^*$, which was shifted in solution to lower energies. The circular dichroism (CD) of the symmetric olefin, whose optical activity is due to dissymmetrically located substituents, originates from the coupling between the electric dipole allowed $\pi \rightarrow \pi^*$ transition and the magnetic dipole allowed $\pi \rightarrow$

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Table I. Transition Energies of the Absorption Spectrum for (4-Methylcyclohexylidene)deuteriomethane (**7**), (4-Methylcyclohexylidene)ethane (**4**), and (4-Methylcyclohexylidene)-2,2,2-trideuterioethane (**5**)

absorption energies, cm^{-1}			
7	**4**	**5**	assignments
49 140	46 340	46 460	$\pi \rightarrow 3s$
50 380	47 730	47 790	$\pi \rightarrow 3s^a$
51 280	49 200	49 110	$\pi \rightarrow \pi^*$
52 630	50 540	50 450	$\pi \rightarrow \pi^* + 1^a$
53 910	51 850	51 780	$\pi \rightarrow \pi^* + 2^a$
56 420	53 230	53 300	$\pi \rightarrow 3p_y$
57 740	55 430	55 325	$\pi \rightarrow 3d$
59 170	57 270	56 980	$\pi \rightarrow 4s$
	58 720	58 520	$\pi \rightarrow 4s^a$
	60 170	59 970	$\pi \rightarrow 4p$
	62 030	62 500	$\pi \rightarrow 4d$
		63 740	$\pi \rightarrow 5s$
		65 470	$\pi \rightarrow 6s$
		66 720	$\pi \rightarrow 7s$

^{a}Assigned to C=C stretching.

$3p_y$ ($\pi \rightarrow \pi_y{}^*$) transition.[3] The proposed[12] sector rule (+XYZ) for the sign of the $\pi \rightarrow \pi^*$ CD signal is obtained by applying either static field or dynamic coupling mechanisms.[3] However, for several molecules it has been shown that the olefin section rule is not obeyed.[3,11,13,15] In some molecules the CD couplet, which should exhibit CD signals of opposite sign for the $\pi \rightarrow \pi^*$ and $\pi \rightarrow \pi_y{}^*$, is not observed.[10]

The absorption and photoelectron spectra of methylenecyclohexane and of ethylidenecyclohexane were measured by Robin and Kuebler.[16] They reported ionization potentials for cyclohexylidenemethane and cyclohexylideneethane of 73500 and 69700 cm^{-1}, respectively. A partial assignment of the absorption spectrum was given by Robin.[16] The assignment was based on term-value arguments. According to Robin the term value of a 3s Rydberg state is dependent on the molecular size and reaches a limit of 22 000–24 000 cm^{-1} for a molecule containing seven to eight carbon atoms.[17] This constant term value was observed for many chromophores including the olefinic functional group. A rich vibrational structure was observed for the Rydberg 3s, the ionic state as well as the $\pi \rightarrow \pi^*$ transition in cyclohexylidenemethane. This structure was attributed to the activity of the C=C symmetric stretch vibrational mode.

In this paper we report our studies on the absorption and the CD spectra of the cyclohexylidenemethane moiety. In particular, we investigated the effect on the CD of various exo vinylic substituents in the (4-methylcyclohexylidene)methane system (**1**). The substituents (X,Y) employed in our study were D, F, Cl, Br, and various alkyl groups. Although bromine and chlorine atoms have excited states absorbing in the wavelength region of this study (2200–1500 Å), a characteristic absorption profile was observed for all the molecules examined. This is the basis for the determination of the role that the substituents play in the optical activity of the chromophore. The purpose of the present study was to determine whether, and in what manner, a substituent lying in the nodal plane of the π orbital contributes to the circular dichroism. Deuterium[18,19] and fluorine[20,21] substituents are known to exhibit an antioctant effect on the $n \rightarrow \pi^*$ transition of the carbonyl chromophore. It is our intention to find whether the same is true for the olefinic chromophore.

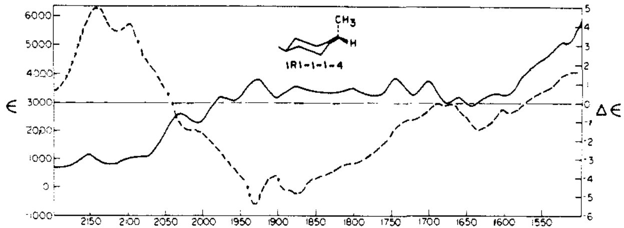


Figure 1. UV (–) and CD spectrum (- -) of (R)-(–)-**4**.

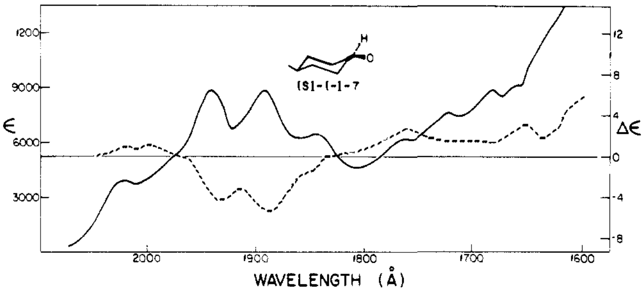


Figure 2. UV (–) and CD spectrum (- -) of (S)-(–)-**7**.

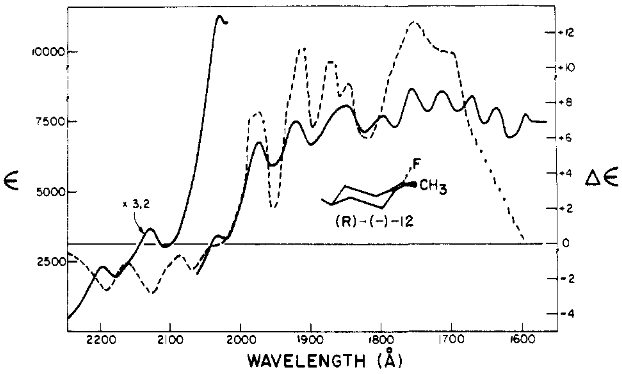


Figure 3. UV (–) and CD spectrum (- -) of (R)-(–)-**12**.

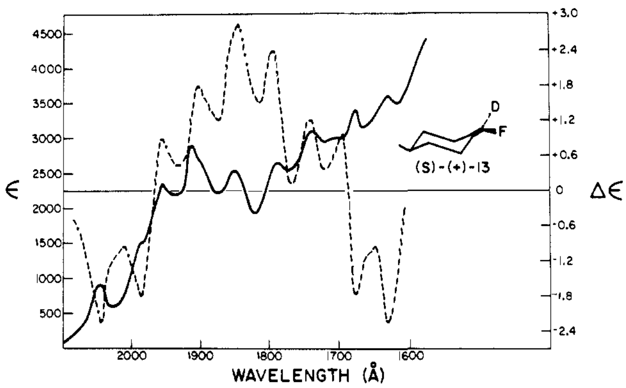
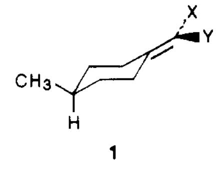


Figure 4. UV (–) and CD spectrum (- -) of (S)-(+)-**13**.



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Results

Syntheses. The syntheses of the chiral (4-methylcyclohexylidene)methane derivatives **1** were accomplished as shown in Schemes I and II.

As one can see from Scheme I the starting point in the syntheses is Gerlach's acid,[22] (R)-(–)-(4-methylcyclohexylidene)acetic acid

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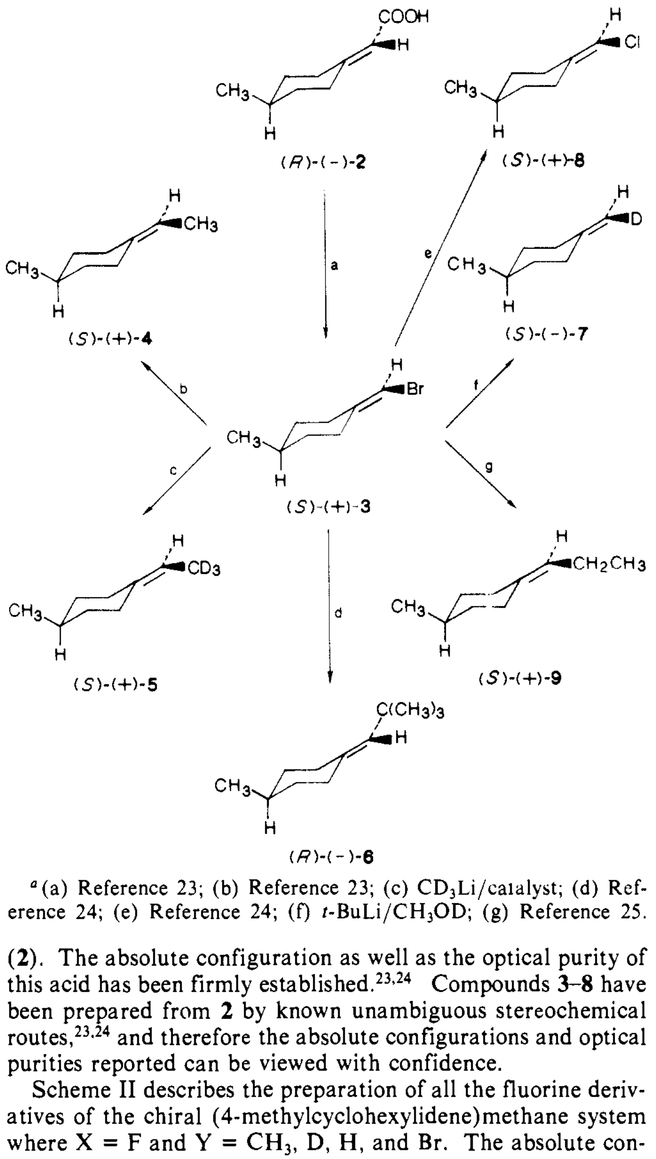
Scheme I[a]



[a] (a) Reference 23; (b) Reference 23; (c) CD_3Li/catalyst; (d) Reference 24; (e) Reference 24; (f) t-BuLi/CH_3OD; (g) Reference 25.

(**2**). The absolute configuration as well as the optical purity of this acid has been firmly established.[23,24] Compounds **3**–**8** have been prepared from **2** by known unambiguous stereochemical routes,[23,24] and therefore the absolute configurations and optical purities reported can be viewed with confidence.

Scheme II describes the preparation of all the fluorine derivatives of the chiral (4-methylcyclohexylidene)methane system where X = F and Y = CH_3, D, H, and Br. The absolute configuration of (−)-(4-methylcyclohexylidene)fluoroacetic acid (**10**) was established to be *S* from the X-ray crystal structure analysis of the amide formed from (−)-**10** and L-(−)-ephedrine.[26] Here again compounds **11**–**13** have the absolute configurations as shown since they are derived from (*S*)-(−)-**10** by reactions of known stereochemistry. Although **11** and **12** are optically pure compounds, **13** and **14** should be viewed as possessing only minimum values for their specific rotations.

Spectra. In Figures 1–4 we show the absorption and CD spectra of compounds **4**, **7**, **12**, and **13** in the gas phase. In Table I we present the assignment of these spectra as well as the data and the assignment of the spectra of (4-methylcyclohexylidene)ethane (**4**) and (4-methylcyclohexylidene)-2,2,2-trideuterioethane (**5**). The three spectra show a striking similarity and are interpretable in the same manner. These spectra are reasonably close to those reported by Robin[16] and others[27] for the symmetric methylenecyclohexane. The assignment of the lower Rydberg states were based on the arguments mentioned above, i.e. term-value arguments. The ionization potential for each molecule was determined by adding 24500 and 23700 cm^{-1} to the energies of the 3s transitions of **7** and **4**, respectively. These term values were taken from Robin's work on the symmetric compounds.[16]

Table II. Energies (cm^{-1}) of the Origin of the 3s State and Its Vibrational Frequency

X	Y	energy of 3s, cm^{-1}	vibrational frequency
H	CD_3	46 460	1330
H	CH_3	46 340	?
H	F	48 840	1670
CH_3	F	45 520	1320
H	Br	48 540	
H	Cl	47 730	
D	F	48 920	
F	Br	47 990	1355
H	D	49 470	

Table III. Energies of the Origin of the $\pi \rightarrow \pi^*$ State and the Frequency of the Leading Vibration

X	Y	energy of $\pi \rightarrow \pi^*$, cm^{-1}	vibrational frequency
H	CD_3	49 110	1330
H	CH_3	49 200	1325
H	F	51 180	1430
CH_3	F	49 120	1550
H	Br	50 125	1430
H	Cl	49 880	1480[a]
D	F	51 180	1480
F	Br	42 440	1445[a]
H	D	51 510	1365

[a] Large fluctuation.

The second transition is assigned as the valence π–π^* band. For all the molecules examined in the gas phase in this study, we have observed opposite sign CD signals for the $\pi \rightarrow 3s$ and $\pi \rightarrow \pi^*$. It is worth noting that among all the chiral olefins studied in the UV-vis in the gas phase[3,9,10,11,15] (~20 molecules), only in one case (β-pinene) did the $\pi \rightarrow 3s$ and $\pi \rightarrow \pi^*$ transitions not show opposite sign CD signals.[3,9] The $\pi \rightarrow 3s$ and the $\pi \rightarrow \pi^*$ exhibit vibrational structure. The two transitions are electric dipole allowed in the symmetric chromophore, and this allows the activity of the C=C symmetric stretching vibration. While for the $\pi \rightarrow 3s$ only two components of this vibration are observed, the $\pi \rightarrow \pi^*$ consists of a progression of three bands belonging to the same vibrations.

Although Hansen and Bouman,[28] in their study of (−)-*trans*-cyclooctene and (*R*)-3-methylcyclopentene, found the π–$3p_x$ and π–$3p_z$ to have lower energies than the π–π^* states,[29] they calculated that for planar olefins such as ethylene and propene[30] the π–π state precedes the π–3p manifold. In our assignment we prefer the classic order of excited states[9,10] in which the π–π^* has a lower energy than the π–3p states.

Replacement of the protons by deuterons in ethylene shifts the positions of the $\pi \rightarrow \pi^*$ and the $\pi \rightarrow 3s$ to higher energies.[31] The magnitude of the isotope shift varies between 200 and 300 cm^{-1} depending on the nature of the transition.[32] In a very detailed investigation of the absorption spectra of ethylene and five deuterium substituted compounds, McDiarmid has also shown that with the introduction of each deuterium atom the origins of the Rydberg states of ethylene is gradually blue-shifted. The blue shift caused by the substitution of a single hydrogen by a deuterium varies from a few to 62 cm^{-1}. In our study the isotope shift observed is 140 cm^{-1} when we compare (4-methylcyclohexylidene)deuteriomethane (**7**) with cyclohexylidenemethane. This blue shift is however, composed both of the contribution of

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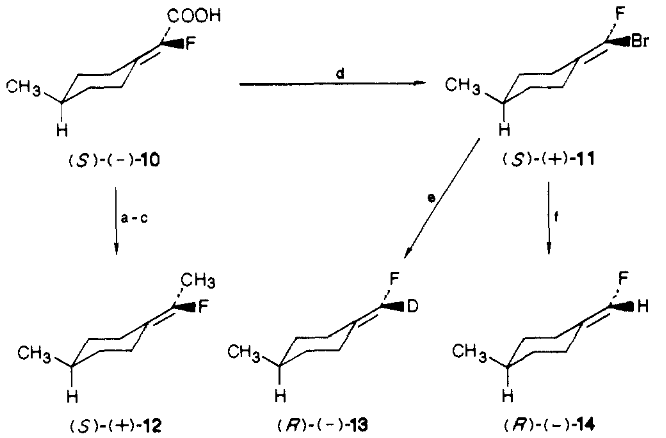
Scheme II[a]



[a] (a) $LiAlH_4$; (b) $CCl_4/(Ph)_3P$; (c) $NaBH_3CN$; (d) Reference 26; (e) Mg/CH_3OD; (f) Mg/CH_3OH.

substituting the hydrogen by the methyl group at position 4 in the cyclohexane ring and the replacement of a vinyl hydrogen by a deuterium atom. The introduction of the methyl group causes a red shift of about 100 cm^{-1}.[16] We are left therefore with a blue shift of ~240 cm^{-1} for the deuterium substitution. This is in good agreement with the isotope shift measured for ethylene.[31] Reasonable isotope shifts are also observed when the methyl hydrogens of **4** are replaced by deuterium atoms as in **5**.

The assignment of the higher Rydberg transitions is based on the Rydberg formula where E_n is the energy of the Rydberg state, IP is the ionization potential, R is the Rydberg constant, and δ is the quantum defect. The ionization potential is determined by adding ~24 000 cm^{-1} to the energy of the 3s state as it is explained below.

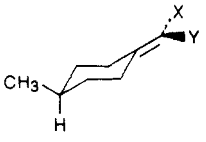
$$E_n = \mathrm{IP} - R/(n - \delta)^2 \qquad (1)$$

In Tables II and III we present the transition energies of the $\pi \rightarrow$ 3s Rydberg and $\pi \rightarrow \pi^*$ valence states from the ground state for all the optically active molecules in this study. We also provide the frequencies of the stretching vibration active in these states. The tables show that the origins of the $\pi \rightarrow$ 3s and $\pi \rightarrow \pi^*$ are constant within less than 3000 cm^{-1}, and the various substituents are only slightly perturbing the excited states of the symmetric chromophore. These results are not surprising since a similar behavior was observed for ethylene where the ionization potential of the homo π electrons is almost constant when the hydrogens in ethylene are gradually substituted to form tetrafluoroethylene.[33] The absorption spectra of the haloethylenes have been shown to be almost a reproduction of the ethylene spectrum.[34]

CD Spectra and Absolute Configurations. With both the CD spectra and absolute configurations of these chiral olefins in hand, it was of interest to ascertain whether a correlation between them could be achieved. Scott and Wrixon[12] have formulated an empirical rule that relates the CD sign of the π–π^* state with the absolute configurations of the chiral olefin. This octant rule works well for many endocyclic but fails for a number of exocyclic olefins.[3,13,14] It is also worth noting, however, that since the CD spectra of the olefins studied by Scott and Wrixon were measured as solutions, the sign of the π–π^* transition might well contain a contribution of the blue-shifted π–3s absorption band, which could effect its sign. In our gas-phase study of the cyclohexylidenemethane system (**1**) we are able to resolve and to identify the CD signals of the π–3s and π–π^* transitions and thereby test, with reliability, the relationship between the CD sign of the π–π^* band and the absolute configuration.

The Scott–Wrixon rule, which is based on Schellman's[35] symmetry treatment, uses the three intersecting planes of symmetry of the alkene to create the octants. The molecular asymmetry of **1** is due solely to having both a substituent other than hydrogen in the 4-position of the cyclohexane ring and that X does not equal Y. Any contribution of allylic axial bonds in **1** would, of course, cancel each other out. In **1** the methyl substituent in the 4-position is kept constant and only the substituents X and Y attached to the double bond are varied. It is therefore, the effect of the X and Y substituents that will determine the sign of the π–π^* signal. In particular we explore the effect of deuterium and fluorine atoms on the π–π^* transitions.

Table IV. Configurations, Atomic Radii, and Sign of π–π^* CD of Various Substituents in **1**



1

configuration	substituent (radii, Å) X	Y	CD (π–π^*) predicted	found
(R)-(−)-**3**	Br (1.14)	H (0.37)	(−)	(−)
(R)-(−)-**4**	CH_3 (0.77)	H (0.37)	(−)	(−)
(R)-(−)-**5**	CD_3 (0.77)	H (0.37)	(−)	(−)
(R)-(+)-**7**	D (0.371)	H (0.373)	(+)	(+)
(R)-(−)-**8**	Cl (0.99)	H (0.37)	(−)	(−)
(R)-(−)-**9**	CH_2CH_3 (0.77)	H (0.37)	(−)	(−)
(R)-(−)-**6**	t-Bu (0.77)	H (0.37)	(−)	(−)
(R)-(−)-**13**	F (0.72)	D (0.371)	(−)	(−)
(R)-(−)-**14**	F (0.72)	H (0.373)	(−)	(−)
(R)-(−)-**11**	Br (1.14)	F (0.72)	(−)	(−)
(R)-(−)-**12**	F (0.72)	CH_3 (0.77)	(+)	(+)

Having a deuterium[36] or fluorine[37] atom at various positions in ketones generates chiroptical contributions that are antioctant. In the olefinic system the role of a deuterium substituent as an isolated perturber is unclear,[38] i.e., (1S)-[1-^{2}H]apobornene exhibits an antioctant behavior whereas (1S)-[2-^{2}H]norbornene obeys the Scott–Wrixon octant rule. In Table IV we summarize the observed CD signs for π–π^* transitions of molecules examined in our study.

It is worth comparing the $\Delta\epsilon/\epsilon$ of the substituted deuterio compounds with other results in which the D atom is responsible for the chirality of the molecule. The $\Delta\epsilon/\epsilon$ measured for the π–π^* of **7** is ~4.4×10^{-4}. For **4**, in which a methyl group replaces one of the vinylic hydrogens, we obtain for the same transition $\Delta\epsilon/\epsilon$ ~ 1.6×10^{-3}. Thus a methyl group shows an optical activity that is only about 4 times greater than the deuterium substituent. This ratio was determined for other chromophores, and it was found to depend not only on the nature of the chromophore but also on various electronic transitions in the chromophore. The $\Delta\epsilon/\epsilon$ ratio for the methyl to deuterium can vary from 36[8] to 3[36c]. The relatively low ratio found in our chromophore is unique and may well be due to the fact that the chirality of molecule **1** is caused by changing the substituents X and Y, both of which are directly attached to the olefinic bond.

All the derivatives of **1** that are included in Table IV have the R configuration. It can be seen that, with the exception of deuterium, when Y = H a negative CD sign is observed for the π–π^* transition. The alkyl substituents as well as the halogens, including fluorine, exhibit the same consignate effect. Attempts to correlate the sign of the CD spectra of the fluorine derivatives with mass or polarizability[39] of the substituents also fails. Although recognizing the danger inherent with making empirical correlations,

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we are inclined to suggest that our results can be rationalized in terms of the C–X vs C–Y bond lengths. The correlation is evident by examining Table IV. When the covalent radius of X > Y, then the CD sign of the π–π^* transition will be negative, and when Y > X it will be positive as long as the substituent X or Y does not possess a π delocalizing system at the point of attachment to C.

Discussion

As we have previously discussed, the replacement of one of the vinylic hydrogens and one of the hydrogens in the 4-position of the cyclohexane ring by another substituent are both necessary and sufficient conditions to cause molecular chirality in the cyclohexylidenemethane system. This chiral system, **1**, provides one with a unique opportunity to evaluate the contribution to the optical activity of a given perturber X relative to a perturber Y that is located across the symmetry plane of the double bond. The comparison between the contributions of various perturbing groups to the rotatory strength has been addressed previously,[7,8,19] and properties such as bond lengths, size, and polarizabilities have been mentioned as important factors.

In the analysis of our results certain reasonable assumptions will be made. We will assume that the double bond is planar and that the substituents X and Y lie in the same plane. Although one could argue that this assumption may not apply to certain large substituents, such as *tert*-butyl, one would agree that it is justified and reasonable for perturbers that are small such as D, H, F, CH_3, etc. We will also assume that the 4-methyl substituent, common to all the molecules in our study, whatever its contribution is, will be the same for all the perturbers X and Y. Therefore, the net effect will be due to these groups.

Of the three leading mechanisms explaining optical activity (static perturbation, dynamic coupling, and the coupled oscillator[40]), two have been applied to the olefin chromophore. The static perturbation mechanism has successfully predicted an octant rule[3] for the sign of the π–π^* signal. However, the substituents that mix the excited states of the symmetric chromophore do not show any dependence on their effective charge[3] or their dipole moment as predicted by theory. This also obtains for the cyclohexylidenemethane chromophore where again no dependence on the dipole moment is observed.

The dynamic coupling mechanism that has been applied to electric dipole allowed transitions by Weigang[4] contains, except for the geometrical factor, a dependence on the anisotropy of the polarizability of the C–C single bond. This negative value, which has also been used by Scott and Yeh,[41] has been questioned by other authors.[3] The geometrical factor, which include octant as well as conical contributions,[4] would show no contributions since the substituents X and Y in cyclohexylidenemethane **1** lie in the nodal surface. It is also worth noting that Weigang's[4] treatment excludes polar perturbers and would therefore not be applicable to halogen substituents.

All three mechanisms have one factor in common, namely, their dependence on R_{C-X}^{-n}, where R_{C-X} is the distance between the chromophore and a substituent X. This distance dependence is introduced in the matrix element of perturbation. Of the three mechanisms, it is the coupled oscillator that exhibits the strongest dependence on R_{C-X} (R_{C-X}^{-2}) and therefore, at first glance, appears to be the best candidate to account for our results. We therefore conclude from our data that if, in Figure 5, $R_{C-X} < R_{C-Y}$ and the coordinates of substituent X are such the X > O and Y < O then the sign of the CD signal will be positive for the π–π^* transition. If, on the other hand $R_{C-X} < R_{C-Y}$ and its coordinates are X > O, Y > O, then a negative signal will be observed. Our observations dictate that the sign of the CD signal of the π–π^* transition is determined by the position of the substituent closest to the olefinic carbon atoms. For example if we consider (*R*)-(+)-**3**, it is the hydrogen that will determine the sign of the π–π^* transition, and since it is located in the X > O, Y > O region, a negative CD signal will be observed.

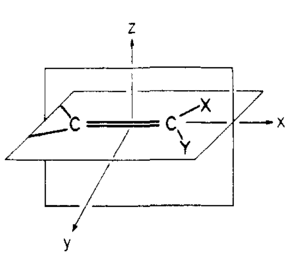

Figure 5. Sectors defining the sign of π–π^* CD absorption of chiral olefins.

Although we have incorporated, in Figure 5 the XY plane (the double-bond plane), the sector rule for the planar double bond is a reduced quadrant rule in which the XZ plane divides the space into positive and negative regions that affect the optical activity of the cyclohexylidenemethane chromophore.

Experimental Section

Melting points were determined with a Mel-temp apparatus. All melting points and boiling points are uncorrected. Infrared (IR) spectra were measured with a Perkin-Elmer Model 257 grating spectrophotometer with a polystyrene 1601 cm^{-1} bond for calibration. Nuclear magnetic resonance (NMR) spectra were recorded on a Brucker 200-MHz or 270-MHz spectrometer. The solvent used was $CDCl_3$ unless noted otherwise, with Me_4Si and $CHCl_3$ (7.26 ppm) as internal standards. The chemical shifts are given in δ (ppm) downfield from Me_4Si, and the coupling constants are in hertz. The microanalyses were performed by Beller Laboratories, Gottingen, West Germany.

The UV–vis CD instrument used in this study has been described previously.[42] The monochromator used for these measurements is a McPherson 225 equipped with a 1200 lines/mm grating yielding a spectra resolution of 8 Å/mm. All the absorption and CD measurements were carried out in a 18-cm cell with use of 2-mm slits. The vapor pressure was measured by a Wallace and Tiernan absolute pressure gauge.

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 accuracy was ±0.002°, and the cell length was 0.4 dm.

Ultraviolet (UV) spectra were recorded with a Cary 219 spectrophotometer. Circular dichroism (CD) spectra were recorded with JASCO Model J-500C spectrophotometer. 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. Wavelengths are reported in nanometers.

For column chromatography, silica gel (70–230 mesh) (Merck) was used unless noted otherwise. Radial chromatography thin-layer separations were performed with Merck silica gel 60 PF_{254} by using Harrison Research Chromatotran Model 7924T.

(*S*)-(–)-(4-Methylcyclohexylidene)deuteriomethane. To a stirred solution of (*S*)-(+)-(4-methylcyclohexylidene)bromomethane $[\alpha]^{20}$ +51.3, (82% optically pure) (6.19 g, 32.8 mmol) in 90 mL of dry ether under an argon atmosphere at –100 °C (methylcyclohexane, liquid nitrogen) was added dropwise a solution of *t*-BuLi (41.0 mL of 1.60 M, 65.6 mmol) in pentane over a period of 25 min. The temperature of the reaction mixture was held at –100 ± 5 °C during the addition. After the addition was completed the solution was maintained at –90 ± 3 °C for a period of 60 min. The light yellow solution was warmed to –75 °C, and 4.0 mL of methanol-*d* (99+% D) was syringed in. The mixture was stirred for 10 min and poured into water, and the organic layer was separated. Removal of the solvent gave a crude product, which was chromatographed with silica gel and eluted with pentane. The fractions corresponding to the pure product were combined, and the solvent was removed to yield, after distillation, 2.13 g (58%) of pure product: bp 57 °C (90 mm); $[\alpha]^{20}$ –0.112 ± 0.002° (*c* 27.2, methanol); IR (neat) 3025 (vinyl C–H), 2275 (vinyl C–D), and 1635 cm^{-1}; ^{1}H NMR (chloroform-*d*) δ 0.92 (d, 3 H), 0.92–2.5 (m, 9 H), and 4.70 (s, 1 H). This sample was homogeneous on GC.

(*R*)-(–)-(4-Methylcyclohexylidene)ethane. To a stirred mixture of dichloro[1,2-bis(diphenylphosphino)ethane]nickel(II) (0.15 g, 0.28 mmol) and (*R*)-(–)-(4-methylcyclohexylidene)bromomethane $[\alpha]^{20}$ –55.8 ± 0.3° [(*c* 1.9, ethanol); 89.7% optically pure] (3.0 g, 15.9 mmol) in 60 mL of dry ether, under an argon atmosphere, was slowly added a solution

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of methyllithium in ether (12.3 mL of 1.50 M, 18.45 mmol). The clear yellow solution was maintained at room temperature (water bath) for 2 h, cooled to 0 °C, and hydrolyzed. The organic phase was diluted with 50 mL of ether and separated from the aqueous phase. The ether solution was washed successively with water, 2 N HCl, and water and dried over potassium carbonate. Removal of the solvent yielded 2.0 g of an oil, which was distilled under reduced pressure to give a colorless liquid: bp 63 °C (36 mm); yield 1.60 g (81%); the product was homogeneous on GC; $[\alpha]^{20}$ −13.15 ± 0.24° (*c* 2.0, chloroform), 74.7% optically pure [lit.[23] $[\alpha]^{20}$ 17.6°]; IR and NMR were identical with that reported: ^{13}C NMR (chloroform-*d*) δ 12.69 (q), 22.16 (q), 27.47 (t), 32.97 (d), 35.86 (t), 36.43 (t), 36.85 (t), 115.18 (d), and 139.71.

(*R*)-(−)-(4-Methylcyclohexylidene)-2,2,2-trideuterioethane. The cross-coupling reaction between (*R*)-(−)-(4-methylcyclohexylidene)bromomethane (89.7% optically pure) with (trideuteriomethyl)lithium was achieved according to the above procedure and yielded, after distillation, (*R*)-(−)-(4-methylcyclohexylidene)trideuteriomethane in 79% yield, bp 63 °C (35 mm). The product was homogeneous on GC: $[\alpha]^{20}$ −12.60 ± 0.25° (*c* 2.0, chloroform), 72% optically pure assuming that the deuterium substitution does not significantly affect the magnitude of rotation; IR (neat) 3000–2800, 2250, 2220, 2140, 2100, and 1660 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.90–2.20 (m including a CH_3 doublet at 0.90, 11 H), 2.57 (br d, 1 H), and 5.20 (br s, 1 H); ^{13}C NMR (chloroform-*d*) δ 22.16 (q), 27.50 (t), 32.97 (d), 35.86 (t), 36.45 (t), 36.45 (t), 36.86 (t), 115.07 (d), and 139.77 (s).

(±)-(4-Methylcyclohexylidene)fluoroacetic Acid. To a stirred solution of trifluorochloroethylene (13.7 g, 0.12 mol) dissolved in a 1.6:1:1 mixture of THF/ether/pentane (200 mL) and cooled to −130 to −110 °C was added a cooled (−70 °C) 2.6 N solution of *n*-butyllithium in hexane (54 mL, 0.14 mol). Stirring was continued at −110 °C for 30 min, and an ethereal solution of 4-methylcyclohexanone (15.5 mL, 0.12 mol) was added. The reaction mixture was hydrolyzed at −70 °C by the addition of 170 mL of 3 N sulfuric acid and allowed to come to ambient temperature. The mixture was extracted with ether, and the ether extracts were washed with water, sodium bicarbonate, and saturated sodium chloride and dried over anhydrous magnesium sulfate. The ether was stripped, and the residue was distilled from sodium bicarbonate (2 g) under vacuum, bp 60–68 °C (0.75 mmHg), to yield 17.5 g of crude (trifluoroethylene)-4-methylcyclohexanol.

The crude alcohol was added to a cooled (−10 °C) solution of concentrated sulfuric acid (60 mL) and water (60 mL), and the mixture was stirred at ambient temperature for 24 h. The reaction mixture was extracted with chloroform, and the extracts were washed with water and dried over magnesium sulfate, and the solvent was removed in vacuo. The crude acid was dissolved in 2 N sodium hydroxide, washed with ether, acidified with 6 N hydrochloric acid, and extracted with ether. The ether extract was dried over anhydrous magnesium sulfate, the solvent was removed in vacuo, and the residue was distilled to yield 14 g (68%) of acid: bp 113–115 °C (0.75 mmHg); IR (film) 3500–2500, 1700, 1650 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.93 (d, *J* = 6 Hz, 3 H), 0.98–2.13 (m, 7 H), 2.94 (br d, *J* = 15 Hz, 1 H), 3.52 (br d, *J* = 14 Hz, 1 H), 7.50 (br s, 1 H). Anal. Calcd for $C_9H_{13}O_2F$: C, 62.77; H, 7.61. Found: C, 62.59; H, 7.57.

Chiral (4-Methylcyclohexylidene)fluoroacetic Acid. To a solution of racemic acid (4.73 g, 0.0275 mol) dissolved in 20 mL of ethyl acetate was added 1.85 mL (1.70 g, 0.014 mol) of (*S*)-(−)-α-phenethylamine. The resulting solid was filtered and recrystallized from ethyl acetate to give 2.9 g of salt, mp 176 °C, $[\alpha]^{20}$ +20.9° (*c* 1.1, EtOH). The salt was dissolved in 2 N sodium hydroxide and washed with ether. The aqueous solution was acidified with 2 N hydrochloric acid and extracted with ether, and the ether extract was dried over anhydrous magnesium sulfate. The solvent was removed in vacuo to yield 1.6 g of acid, $[\alpha]^{20}$ +39° (*c* 1.1, EtOH).

Via the procedure described for the (+) acid, the free acid (2.4 g, 0.04 mol) obtained from the mother liquors was treated with 1.7 g (0.14 mol) of (*R*)-(+)-α-phenethylamine. The salt was recrystallized from ethyl acetate to give 2.6 g of salt, mp 180 °C, $[\alpha]^{20}$ −20.6° (*c* 1.1, EtOH), which upon workup yielded 1.5 g of acid, $[\alpha]^{20}$ −41.3° (*c* 1.1, EtOH). The IR and ^{1}H NMR spectra of the chiral acids were identical with those of racemic (4-methylcyclohexylidene)fluoroacetic acid.

Methyl (±)-(4-Methylcyclohexylidene)fluoroacetate. A solution of (±)-(4-methylcyclohexylidene)fluoroacetic acid (4.9 g, 0.028 mol) in 10 mL of diethyl ether was cooled to 0 °C, and freshly distilled diazomethane was added until the yellow color persisted. The reaction mixture was filtered through 10 g of silica gel, and the solvent was removed to give pure methyl (±)-(4-methylcyclohexylidene)fluoroacetate (5.15 g yield, 98.8%): ^{1}H NMR δ 0.93 (d, 3 H), 0.98–2.10 (m, 7 H), 2.90 (br d, *J* = 11.2 Hz, 1 H), 3.50 (br d, *J* = 14.4 Hz, 1 H), 3.78 (s, 3 H); IR (film) 1733 (s), 1660 (m) cm^{-1}. Anal. Calcd for $C_{10}H_{15}O_2F$: C, 64.52; H, 8.06. Found: C, 64.46; H, 8.13.

Methyl (*R*)-(+)-(4-Methylcyclohexylidene)fluoroacetate. (*R*)-(+)-(4-methylcyclohexylidene)fluoroacetic acid was esterified as described above to give the product: $[\alpha]^{23}$ +56.00 ± 0.03° (*c* 0.11, C_2H_5OH; UV (λ_{226nm}) ε 16 840 (*c* 7.84 × 10^{-5}, cyclohexane); CD (λ_{225nm}) Δε +2.67 (7.84 × 10^{-5}, cyclohexane).

(±)-(4-Methylcyclohexylidene)fluoroethanol. To a solution of $LiAlH_4$ (2.47 g, 0.67 mol) in 80 mL of diethyl ether was added a solution of $AlCl_3$ (3.01 g, 0.023 mol) in 50 mL of ether at 0 °C, and the reaction mixture was stirred for 1 h. An ethereal solution of methyl (±)-(4-methylcyclohexylidene)acetate (4.2 g, 0.23 mol) was added dropwise at 0 °C, and stirring was continued for 1 h. The reaction mixture was hydrolyzed with wet Na_2SO_4 and filtered, and the solvent was evaporated. The crude product was purified by passing through a silica gel column with CH_2Cl_2. Removal of the solvent gave pure (±)-(4-methylcyclohexylidene)fluoroethanol, 3.0 g (yield, 84%): ^{1}H NMR δ 0.91 (d, 3 H), 0.95–1.98 (m, 8 H), 2.38 (br d, *J* = 14 Hz, 1 H), 2.81 (br d, *J* = 14 Hz, 1 H), 4.26 (dd, 2 H); IR (film) 3300 (br s), 1700 (m) cm^{-1}.

(*R*)-(−)-(4-Methylcyclohexylidene)fluoroethanol. The compound was prepared by using the same procedure as for the racemic compound. Methyl (*R*)-(+)-(4-methylcyclohexylidene)fluoroacetate was used to give product with $[\alpha]^{23}$ −35.30 ± 0.03° (*c* 0.11, C_2H_5OH).

(±)-(4-Methylcyclohexylidene)-1-fluoro-2-chloroethane. A solution of (±)-(4-methylcyclohexylidene)fluoroethanol (0.87 g, 0.006 mol) and triphenylphosphine (1.73 g, 0.007 mol) in 5 mL of carbon tetrachloride was kept at ambient temperature for 48 h. The reaction mixture was diluted with 2 mL of pentane, cooled to 0 °C, and filtered. The solvent was removed, and the crude product was placed on a silica gel column and eluted with pentane. The solvent was removed, and the residue was purified by using radial chromatography to give pure (±)-(4-methylcyclohexylidene)-1-fluoro-2-chloroethane (0.603 g, yield 61.8%): ^{1}H NMR δ 0.92 (d, 3 H), 0.94–2.18 (m, 7 H), 2.35 (br d, *J* = 14.2 Hz, 1 H), 2.81 (br d, *J* = 14.7 Hz, 1 H), 4.19 (d, *J* = 22.4 Hz, 2 H); IR (film) 2940 (s), 2900 (s), 2840 (s), 1690 (m), 1450 (s), 1290, 885 cm^{-1}. Anal. Calcd for $C_9H_{14}ClF$: C, 61.19; H, 7.93. Found: C, 61.38; H, 7.92.

(*R*)-(−)-(4-Methylcyclohexylidene)-1-fluoro-2-chloroethane. Prepared by using the same procedure as for the racemic compound. (*R*)-(−)-(4-methylcyclohexylidene)fluoroethanol ($[\alpha]^{23}$ −35.30) was used as starting material to give product, $[\alpha]^{23}$ −32.02 ± 0.01° (*c* 0.11, C_2H_5OH) in 67% yield: UV (λ_{208nm}) ε 12 330 (*c* 9.57 × 10^{-5}, cyclohexane); CD $\Delta\epsilon_{213}$ −0.25 (*c* 3.83 × 10^{-4}, cyclohexane).

(±)-(4-Methylcyclohexylidene)fluoroethane. A solution of (±)-(4-methylcyclohexylidene)-1-fluoro-2-chloroethane (0.380 g, 2.16 mmol) and sodium cyanoborohydride (0.550 g, 8.80 mmol) in 6 mL of hexamethylphosphoramide was stirred for 3 days at 70 °C. The reaction mixture was diluted with 10 mL of water and extracted with ether. The ether extract was washed with water and dried over anhydrous sodium sulfate. The solvent was removed, and the residue was purified by radial chromatography to give pure (±)-(4-methylcyclohexylidene)fluoroethane (0.110 g, yield 35.9%): ^{1}H NMR δ 0.88 (d, 3 H), 0.92–1.90 (m, 7 H), 1.87 (dm, *J* = 17.9 Hz, 3 H, 3 H), 2.23 (br d, *J* = 17.3 Hz, 1 H), 2.78 (br d, *J* = 16.4 Hz, 1 H); IR (film) 2940 (s), 2900 (s), 2840 (s), 1708 (m), 1445 (m), 1385 (m), 1165, 910 cm^{-1}. Anal. Calcd for $C_9H_{15}F$: C, 76.06; H, 10.56. Found: C, 76.24; H, 10.69.

(*R*)-(−)-(4-Methylcyclohexylidene)fluoroethane. The compound was prepared via the procedure used for the racemic compound. (*R*)-(−)-(4-Methylcyclohexylidene)-1-fluoro-2-chloroethane, $[\alpha]^{20}$ −32.02 ± 0.01° (*c* 0.11, C_2H_5OH) was used to give (*R*)-(−)-(4-methylcyclohexylidene)fluoroethane, $[\alpha]^{18}$ −25.5 ± 0.02°, in 36% yield: UV (λ_{198nm}) ε 8730 (*c* 1.077 × 10^{-4}, cyclohexane); CD $\Delta\epsilon_{210}$ −0.139 (*c* 4.31 × 10^{-4}, cyclohexane).

(±)-(4-Methylcyclohexylidene)bromofluoromethane. To a solution of 10.32 g (0.06 mol) of (*RS*)-(4-methylcyclohexylidene)fluoroacetic acid in 20 mL of $CHCl_3$ at −70 °C was added 9.6 g (0.06 mol) of bromine dissolved in 20 mL of dichloromethane. The reaction mixture was stirred at room temperature overnight. The decolorized reaction mixture was slowly added to a solution of 32 g of sodium carbonate in 50 mL of water while steam was being passed through the solution. The steam distillate was collected, and the methylene chloride phase was separated. The aqueous solution was extracted with ether, and the combined extracts were dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure to yield an oil, which was distilled from anhydrous sodium carbonate to yield 6.8 g (55%) of product: bp 66–68 °C (15 mmHg); IR (film) 3000–2800, 1800, 1675, 1450 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.91 (d, *J* = 6.5 Hz, 3 H), 1.15–2.00 (m, 7 H), 2.39 (d, *J* = 15 Hz, 1 H), 2.81 (d, *J* = 13 Hz, 1 H). Anal. Calcd for $C_8H_{12}FBr$: C, 46.40; H, 5.84. Found: C, 46.51; H, 5.83.

(*S*)-(+)-(4-Methylcyclohexylidene)bromofluoromethane. To a solution of 4.14 g (0.024 mol) of (*S*)-(4-methylcyclohexylidene)fluoroacetic acid $[\alpha]^{20}$ −41.30° (*c* 1.1, ethanol) dissolved in 10 mL of $CHCl_3$ at −70 °C was added a solution 1.23 mL (0.024 mol) of bromine dissolved in

J. Am. Chem. Soc. 1988, 110, 4599–4602

20 mL of dichloromethane. The reaction mixture was allowed to reach ambient temperature, and stirring was continued overnight. The decolorized reaction mixture was slowly added to a solution of 15 g of sodium carbonate in 30 mL of water while steam was being passed through the solution. The steam distillate was collected, and the organic phase was separated. The aqueous solution extracted with ether, and the combined extracts were dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure to yield an oil, which was distilled from anhydrous sodium carbonate to yield 2.58 g (52%) of product: bp 68 °C (15 mmHg); $[\alpha]^{20}$ +13.06° (*c* 1.1, ethanol).

(*R*)-(−)-(4-Methylcyclohexylidene)fluoromethane. To a solution of 7.76 g (0.0375 mol) of (*S*)-(+)-(4-methylcyclohexylidene)bromofluoromethane, $[\alpha]^{20}$ +13.06° (*c* 1.1, ethanol), and 1.08 mL (0.012 mol) of 1,2-dibromoethane in 130 mL of methanol was added 18 g (0.75 mol) of magnesium. CO_2 was continuously passed through the reaction mixture during the course of the reaction. After an induction period, a very vigorous exothermic reaction ensued. The resultant slurry was stirred at 65 °C for 1.5 h, and the unreacted magnesium was separated by centrifugation and washed with 20 mL of methanol and then pentane (2 × 50 mL). The combined organic extract was acidified with 6 N HCl at 0 °C and extracted with pentane (5 × 100 mL). The combined extracts were washed with water and dried over $MgSO_4$. The solvent was removed by distillation through a spinning-band distillation column (pot temperature, 50 °C; column temperature, 45 °C). Distillation of the residue gave 3.2 g (68%) of pure product: bp 115–116 °C; $[\alpha]^{20}$ −38.6° (*c* 1.1, ethanol); UV (*c* $1.6.10^{-4}$, cyclohexane) ($\lambda_{196\mathrm{nm}}$) ϵ 6250; CD (*c* 1.6×10^{-4}, cyclohexane) $\Delta\epsilon_{200}$ +2.44; IR (film) 1670 cm^{-1}; ^1H NMR δ 0.90 (d, $J = 7$ Hz, 3 H), 0.92–1.95 (m, 7 H), 2.00–2.11 (m, 1 H), 2.71–2.82 (m, 1 H), 6.38 (d, $J = 88$ Hz, 1 H); ^{19}F NMR δ ($CF_3C_6H_5$ ref = 0 ppm) −78.17 (d, $J = 87$ Hz). Anal. Calcd for $C_8H_{13}F$: C, 74.96; H, 10.22. Found: C, 74.87; H, 10.19.

(*S*)-(+)-(4-Methylcyclohexylidene)fluorodeuteriomethane. To a solution of 5.18 g (0.025 mol) of (*R*)-(−)-(4-methylcyclohexylidene)-bromofluoromethane, $[\alpha]^{20}$ −12.7° (*c* 1.1, ethanol), and 0.72 mL (0.008 mol) 1,2-dibromoethane in 85 mL of methanol-*O-d* was added 12.1 g (0.5 mol) of magnesium. CO_2 was passed continuously through the reaction mixture during the course of the reaction. After an induction period, a very vigorous exothermic reaction ensued. The resultant slurry was stirred at 65 °C for 1.5 h, and the unreacted magnesium was separated by centrifugation and washed with 20 mL of methanol and then pentane (2 × 50 mL). The combined organic extract was acidified with 6 N HCl at 0 °C and then extracted with pentane (5 × 100 mL). The combined extracts were washed with water and dried over $MgSO_4$. The solvent was removed by distillation through a spinning-band distillation column (pot temperature, 50 °C; column temperature, 45 °C). Distillation of the residue gave 2.2 g (69%) of pure product: bp 115–116 °C; $[\alpha]_{Hg}$ +39.6° (*c* 1.1, ethanol); UV (*c* 1.43×10^{-4}, cyclohexane) (λ_{194}) ϵ 6700; CD (*c* 1.43×10^{-4}, cyclohexane) $\Delta\epsilon_{201}$ −1.56; IR (film) 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (d, $J = 7$ Hz, 3 H), 0.92–1.95 (m, 7 H), 2.00–2.11 (m, 1 H), 2.71–2.82 (m, 1 H). Anal. Calcd for $C_8H_{12}DF$: C, 74.38; HD, 10.90. Found: C, 74.14; HD, 10.57.

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Pentacoordinate Allylsilicates: Characterization and Highly Stereoselective Reaction with Aldehydes[1]

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Abstract: Lithium and bis(triphenylphosphoranylidene)ammonium salts of bis(1,2-benzenediolato)allylsilicates, which were prepared via the reactions of allyl-, prenyl-, and (*E*)- and (*Z*)-crotyltrichlorosilanes with dilithium catecholate, were found to react with aromatic aldehydes chemoselectively to give the corresponding homoallyl alcohols in a regiospecific and highly diastereoselective manner in high yields. The unique reaction modes including the diastereoselectivity are interpreted by a six-membered cyclic transition state, which is favored by the enhanced nucleophilicity of the γ-carbon of the allylsilicates as well as by the significant Lewis acidity giving hexacoordinate silicates. In contrast, however, allylsilicates with α,α-bis(trifluoromethyl)benzenemethanolato(2−)-C^2,*O* ligands did not react with the aldehydes. The inertness may be attributable to the rather rigid trigonal-bipyramidal structure with low Lewis acidity.

Although allylation of carbonyl compounds with allyltrimethylsilanes promoted by fluoride ions has been well established as a useful synthetic method for homoallyl alcohols,[2,3] the reaction mechanism is still unclear. In our previous paper,[2] we suggested that an allylic carbon–silicon bond is cleaved by fluoride ions to generate an allyl anion that adds to carbonyl compounds on the basis of the substantial difference in the values of Si–C and Si–F bond strength as well as the low regiospecificity of the reaction. More recently, Majetich et al.[3] proposed pentacoordinate allylsilicate intermediates formed from fluoride ion addition to silicon as an ambient nucleophilic species. However, nothing had been known about pentacoordinate allylsilicates before we initiated the present study,[4] whereas a number of pentacoordinate organosilicates have been well characterized.[7] After completion of this work,[8] we became aware of the closely related studies on the pentacoordinate allylsilicates by Corriu et al.[9] and by Hosomi et al.[10] We report here the characterization of several pentacoordinate allylsilicates and their unique reactivity toward carbonyl compounds. In contrast to allyl anions, pentacoordinate allylsilicates were found to react with aldehydes chemoselectively to give the corresponding homoallyl alcohols in regiosepecific and highly stereoselective manner. The reaction modes of penta-

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