nitrobenzene was not determined. The disappearance of ca. 25 mM nitrobenzene was observed by IR; the disappearance of greater than stoichiometric amounts is to be expected because $Cp_2W_2(CO)_6$ and $Cp_2W_2(CO)_5PPh_3$, the expected organometallic products from this reaction, react with nitrobenzene to give non-carbonyl-containing products.[32] Significantly, control experiments showed that $CpW(CO)_3^-$ does not react with nitrobenzene under the conditions of our experiment.

In order to explore the scope of and provide confirmatory evidence for phosphoranyl radicals as reducing intermediates in organometallic reactions, we carried out, in the presence of PPh_3, a reaction known to produce radicals, namely, the photolysis of $Cp_2W_2(CO)_6$ in the presence of organohalide (see Scheme III). Phenyl iodide was chosen as the organic radical precursor because of its lack of susceptibility toward nucleophilic substitution by either PPh_3 or $CpW(CO)_3^-$[33] and because the phenyl radical would be expected to form a stable phosphoranyl adduct. Results consistent with formation and subsequent oxidation of $\cdot PPh_4$ were obtained: irradiation under a CO atmosphere ($\lambda > 500$ nm) of a phenyl iodide solution of $[CpW(CO)_3]_2$ (10 mM) and PPh_3 (0.4 M) afforded $CpW(CO)_3^-$ (5 mM, 50% based on Scheme III), $CpW(CO)_2(PPh_3)I$, small amounts of $CpW(CO)_3I$, and no organometallic cation as monitored by IR. PPh_4^+ was identified by adding cyclohexane to the reaction solution and then dissolving the resulting precipitate in acetone-d_6. The resulting ^1H NMR spectrum showed the characteristic multiplet of the PPh_4^+ species (7.83–7.90 ppm), which was identical with that of an authentic sample of PPh_4I. Scheme III explains these results and products.

Conclusion

At a first glance, Schemes I and II seem unrelated to a mechanism we have recently reported for disproportionation of metal–metal bonded dimers (see Scheme I, ref 6). However, the Me radical is isolobal to the $CpMo(CO)_3$ and $CpMo(CO)_2L$ fragments and thus the reactants and products of eq 4 and the dimer disproportionation reactions are "isolobal" (more specifically they are comprised of isolobal fragments). But what is most important, the key intermediate in Schemes I and II, PPh_3Me, is isolobal to the 19-electron intermediate, $CpMo(CO)_2L_2$, formed in the disproportionation reactions. Schemes I and II are thus *mechanistically isolobal* to the disproportionation pathway. In drawing this comparison between apparently unrelated reactions, we seek not only to point out the utility of the isolobal concept in mechanistic chemistry but also to alert mechanistic chemists to what we believe may be a far more general phenomenon, namely, the intermediacy of electronically "super-saturated" species as reductants.

Acknowledgment is made to the National Science Foundation and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this work. We thank Prof. P. Wagner for communicating the results in ref 13 prior to publication.

Supplementary Material Available: Elaboration of the conclusions presented in the section entitled Conclusions Derived from Tests for Alternative Mechanisms (9 pages). Ordering information is given on any current masthead page.

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Vibrational Circular Dichroism of Phenylcarbinols. A Configurational Correlation

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Abstract: The vibrational circular dichroism (VCD) spectra of enantiomers of phenylcarbinols were studied in the 1600–800 cm^{-1} region. In these molecules, the PhC(OH)H group is a common structural feature, and the chirality of this probe group correlates with the sign of a VCD band at about 1200 cm^{-1}. Viewing the probe group with the fourth ligand behind it, a clockwise arrangement of the probe group substituents (with the usual sequence rule priority, OH > Ph > H), designated as a clockwise probe group chirality, results in a negative sign for the VCD band at about 1200 cm^{-1}. For a counterclockwise probe group chirality, the VCD band is positive. On the basis of infrared and Raman spectral observations with deuterated analogues, this band is assigned to a *C–H deformation mode of the phenylcarbinols.

Vibrational circular dichroism (VCD) and Raman optical activity (ROA) are two types of vibrational optical activity (VOA) that have emerged in the past decade.[1-3] In order to realize the full potential of VOA in elucidating the configurations and conformations of chiral molecules, correlations relating VOA spectral features to known structural and stereochemical details need to be found. The antisymmetric stretching and deformation modes of the methyl group were predicted[4-6] to have bisignate VOA features with the respective signs reflecting the configuration at the chiral center to which the methyl group is attached. In this context, the VOA studies of enantiomers of α-phenylethylamine, α-phenylethyl alcohol, and deuterated α-phenylethanes have attracted much attention.[7-10] As a continuation of our previous

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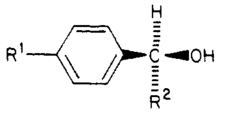
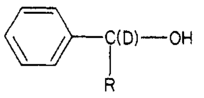
Table I. Phenylcarbinols Used for Spectral Measurements

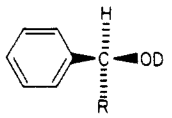
compd	name	$[\alpha]^{23-25}_{D}$, deg	% ee	% D[a]	ref[b]
(*S*)-**1**	(*S*)-benzyl-α-*d* alcohol	+1.32[c]	74	>95	14
(±)-**1**	(±)-benzyl-α-*d* alcohol			>95	
(*R*)-**2**	(*R*)-1-phenylethanol	+39.1[c]	87		15
(*S*)-**3**	(*S*)-1-(*p*-chlorophenyl)ethanol	−54.0[c]	94		16, *d*
(*S*)-**4**	(*S*)-1-(*p*-(trifluoromethyl)phenyl)ethanol	−41.0[e]	90		*d*
(*R*)-**5**	(*R*)-mandelic acid[f]	−153[g]	100[h]		17
(*S*)-**5**	(*S*)-mandelic acid[i]	+151[g]	98[h]		17
(*R*)-**6**	methyl (*R*)-mandelate[f]	−169[k]	95[j]		17
(*S*)-**6**	methyl (*S*)-mandelate[i]	+166[k]	94[j]		17
(±)-**7**	(±)-**1**-phenylethanol-**1**-*d*			>95	
(±)-**8**	(±)-mandelic-α-*d* acid			>95	
(±)-**9**	(±)-1-phenylethanol-*O*-*d*			85	
(±)-**10**	methyl (*R*)-mandelate-*O*-*d*[f]			75	

[a] Based on ^{1}H NMR spectral measurement. [b] For absolute configuration and the basis for the estimation of % ee. [c] Neat. [d] This work. [e] Observed rotation: neat, 1 dm. [f] Equivalent to the D configuration. [g] 2.00–2.09 g/100 mL of absolute C_2H_5OH. [h] On the basis of the rotatory power in ref 17 for (*R*)-**5** corresponding to 100% ee. [i] Equivalent to the L configuration. [j] *c* 1.42–1.56 g/100 mL of $CHCl_3$. [k] On the basis of the rotatory power in ref 17 for (*S*)-**6** corresponding to 100% ee.

work,[10] we now report VCD measurements with enantiomers of some phenylcarbinols (**1–6**) with the aim to explore the relationship of their structure and chirality to the sign of their VCD bands below 1400 cm^{-1}.


(*S*)-**1**, R^1=H; R^2=D
(*S*)-**2**, R^1=H; R^2=CH_3
(*S*)-**3**, R^1=Cl; R^2=CH_3
(*S*)-**4**, R^1=CF_3; R^2=CH_3
(*R*)-**5**, R^1=H; R^2=CO_2H
(*R*)-**6**, R^1=H; R^2=CO_2CH_3


(±)-**7**, R=CH_3
(±)-**8**, R=CO_2H


(*S*)-**9**, R=CH_3
(*R*)-**10**, R=CO_2CH_3

The VCD of an enantiomer of benzyl-α-*d* alcohol (**1**) is of special interest as the chirality of **1** arises as the result of isotope substitution. Barron[11] reported the ROA of (*S*)-benzyl-α-*d* alcohol [(*S*)-**1**] with a bisignate couplet at about 900 cm^{-1} attributed to the *C–D deformation modes. The VCD of an enantiomer of **1**, however, has not been previously reported, and earlier VCD measurements with chiral phenylcarbinols have been limited in most cases[2,3,12,13] to the 3500–2500 cm^{-1} region and in some cases[8] down to 1400 cm^{-1}.

Significantly, this present work reveals a striking relationship of the absolute configurations of the phenylcarbinols **1–6** with the sign of the VCD band at about 1200 cm^{-1}. On the basis of the infrared and Raman spectral observations with the deuterated compounds **7–10**, this band is assigned to a *C–H deformation mode of the phenylcarbinols.

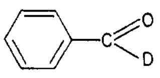
Results and Discussion

Synthesis and Absolute Configurations. The phenylcarbinols used for spectral measurements are shown in Table I together with their respective enantiomeric purities and percent deuterium incorporations.

Table II. Physical Properties of *p*-Nitrobenzoates

			spectra, λ_{max}, nm (ϵ or $[\theta]$[a])	
compd	mp, °C	$[\alpha]^{25-26}_{D}$,[b] deg	EA	CD
(±)-**12**[c]	42–43			
(*R*)-**12**[d]	oil	−49	259 (15 000)	261 (−14 000)
(*S*)-**13**[e]	58–59	+32	259 (15 000)	261 (+15 000)
(*S*)-**14**[f]	69–70	+40	259 (15 000)	260 (+15 000)

[a] Molecular ellipticity. [b] 0.88–1.20 g/100 mL of C_6H_6. [c] Lit.[22] mp 42.5–43.5 °C. [d] Infrared spectrum of a liquid film identical with that of (±)-**12** as a dispersion in KBr. [e] Anal. Calcd for $C_{15}H_{12}ClNO_4$: C, 58.93; H, 3.96. Found: C, 59.00; H, 4.04. [f] Anal. Calcd for $C_{16}H_{12}F_3NO_4$: C, 56.64; H, 3.57. Found: C, 56.79; H, 3.80.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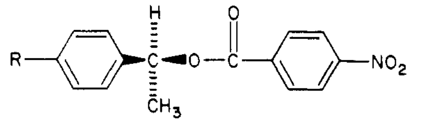
(*S*)-**12**, R=H
(*S*)-**13**, R=Cl
(*S*)-**14**, R=CF_3

(*S*)-Benzyl-α-*d* alcohol[14] [(*S*)-**1**] was prepared by the reduction of benzaldehyde-*1*-*d*[18] (**11**) with *B*-3-pinanyl-9-borabicyclo[3.3.1]nonane (3-pinanyl-9-BBN). The enantiomers of 1-phenylethanol[15] (**2**), mandelic acid[17] (**5**), and methyl mandelate[17] (**6**) were from outside sources, but (±)-1-(*p*-chlorophenyl)ethanol[19] [(±)-**3**] and (±)-1-(*p*-(trifluoromethyl)phenyl)ethanol[20] [(±)-**4**] were prepared by reduction of the corresponding acetophenones. Resolution of the carbinols by fractional crystallization of the (*S*)-α-phenylethylamine salts of the respective acid phthalate esters gave the enantiomers. The racemic deuteriophenylcarbinols [(±)-**1,7,8**] were prepared by reduction of the respective carbonyl compounds with lithium aluminum deuteride or sodium borodeuteride and the *O*-deuterio compounds [(±)-**9** and (*R*)-**10**] by exchange in deuterium oxide.

The absolute configurations of the enantiomers of **1**, **2**, **5**, and **6** were assigned earlier (Table I), but those of the enantiomers of the para-substituted phenylcarbinols [(*S*)-**3,4**] have not been previously reported. The absolute configuration of (*S*)-**3** was established by its conversion on hydrogenolysis to (*S*)-**2** while that of (*S*)-**4** was assigned by comparison of the electronic circular dichrosim (CD) spectrum of the *p*-nitrobenzoyl derivatives (*R*)-**12**

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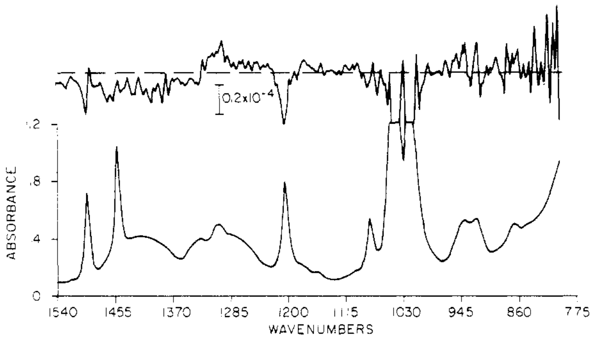

Figure 1. Fourier transform infrared absorption (bottom trace) and circular dichroism (VCD) (top trace) spectra of (*S*)-benzyl-α-*d* alcohol [(*S*)-**1**] as the neat liquid.

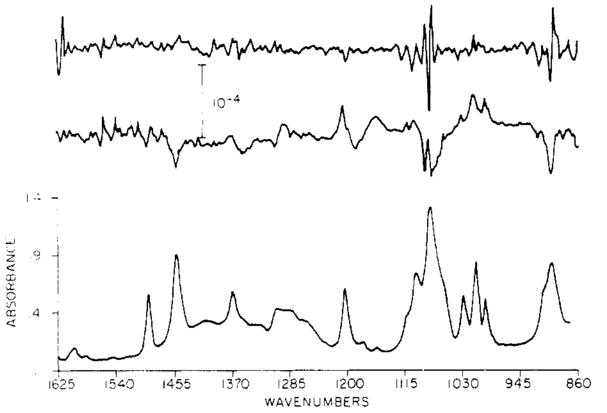

Figure 2. Fourier transform infrared absorption (bottom trace) and circular dichroism (VCD) (middle trace) spectra of (*R*)-1-phenylethanol [(*R*)-**2**] as the neat liquid. The top trace is the difference between two individual VCD observations and provides an estimate of spectral reproducibility.

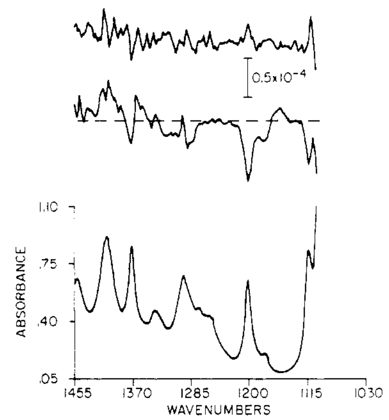

Figure 3. Fourier transform infrared absorption (bottom trace) and circular dichroism (VCD) (middle trace) spectra of (*S*)-1-(*p*-chlorophenyl)ethanol [(*S*)-**3**] as the neat liquid. The top trace was determined the same way as the top trace in Figure 2.

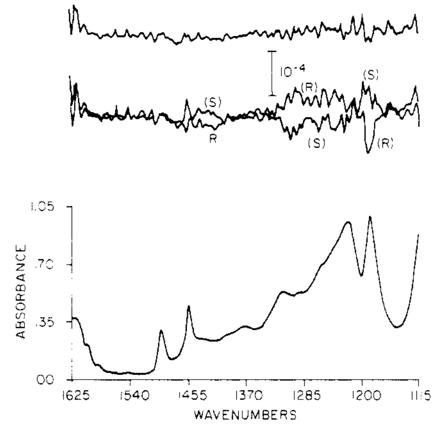

Figure 4. Fourier transform infrared absorption spectrum for (±)-mandelic acid [(±)-**5**] (bottom trace) and circular dichroism (VCD) (middle traces) spectra of (*R*)- and (*S*)-mandelic acid [(*R*)- and (*S*)-**5**] as 0.5 M solutions in dimethyl-d_6 sulfoxide. The top trace is one-half of the sum of the raw VCD spectra of the enantiomers minus the VCD spectrum of the racemate and represents the noise level in the VCD measurements.

Table III. Vibrational Circular Dichroism Correlation

compd	VCD band		probe group chirality[b]
	position, cm^{-1}	g[a] × 10^4	
(*S*)-**1**	1204[c]	−0.4	CW
(*R*)-**2**	1205[c]	+1.0	CCW
(*S*)-**3**	1201[c]	−1.0	CW
(*S*)-**4**	1205[c]	–[d]	CW
(*R*)-**5**	1187[e]	−0.5	CW
(*S*)-**5**	1187[e]	+0.5	CCW
(*R*)-**6**	1187[f]	−0.4	CW
(*S*)-**6**	1187[f]	+0.4	CCW

[a] Dissymmetry factor which equals $\Delta A/A$ where A is the isotropic absorption and $\Delta A = A_l - A_r$. A_l and A_r are the absorbances of left and right circularly polarized light, respectively. [b] This chirality refers to that of the probe group, PhC(OH)H, by considering the OH, Ph, and H groups in decreasing order of priority and the fourth group remote from the observer. [c] Neat. [d] Magnitude for this negative band is uncertain because of the noise associated with the absorption of the trifluoromethyl group. [e] In dimethyl-d_6 sulfoxide. [f] In carbon tetrachloride.

and (*S*)-**13** of (*R*)-**2** and (*S*)-**3**, respectively, with the *p*-nitrobenzoyl derivative of (*S*)-**4**. The *p*-nitrobenzoyl chromophore in these derivatives shows a strong electronic absorption (EA) maximum at 259 nm[21] (Table II) giving rise to a strong Cotton effect, the sign of which correlates with their absolute configurations.

This CD application is an extension of the circular dichroic exciton chirality method[23,24] as applied to the benzoate derivatives of acyclic, chiral allylic alcohols by Gonnella, Nakanishi, Martin, and Sharpless.[21] In the present application, the ^1L_a and ^1B_a $\pi \rightarrow \pi^*$ transitions, lying below 220 nm, of the benzene ring in the carbinol moiety couple with the charge-transfer transition at about 260 nm of the *p*-nitrobenzoate group giving rise to a Cotton effect at 260 nm, negative for (*R*)-**12** and positive for (*S*)-**13** (Table II). By comparison, the *S* configuration is assigned to the enantiomer of 1-(*p*-(trifluoromethyl)phenyl)ethanol (**4**) whose *p*-nitrobenzoate derivative shows a positve Cotton effect at 260 nm.

For conformationally mobile chiral *p*-nitrobenzoate derivatives such as **12**–**14**, it is difficult to deduce the overall chirality of the dipole–dipole coupling of the ^1L_a and ^1B_a transitions of the benzene ring with the charge-transfer transition of the benzoate chromophore. The respective conformational distribution, and thus the overall dipole–dipole coupling, can safely be assumed to be the same for the *p*-nitrobenzoate derivatives of analogous phenylalkylcarbinols of a particular configuration but differing in structure only by a substituent on the benzene ring. Further, as with the *N*-salicylidene derivatives of chiral α-phenylalkylamines,[25] substitution at various positions on the benzene ring of an enantiomer of 1-phenylethanol should have little effect on the Cotton effect of its *p*-nitrobenzoate derivative.

Vibrational Circular Dichroism. The VCD spectrum of (*S*)-benzyl-α-*d* alcohol [(*S*)-**1**] is shown in Figure 1 in which a strong VCD feature is found to be associated with the absorption band

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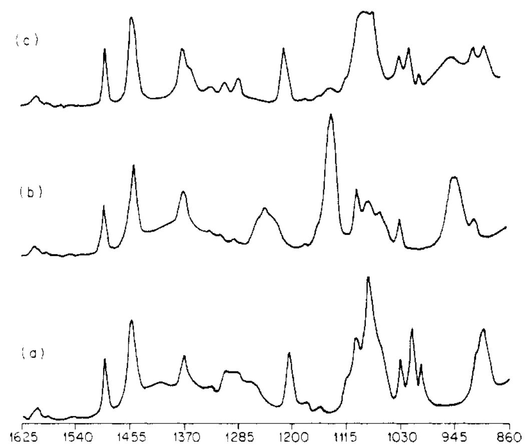
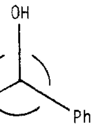


Figure 5. Fourier transform infrared absorption spectra of (a) (±)-1-phenylethanol, (b) (±)-1-phenylethanol-*1-d*, and (c) (±)-1-phenylethanol-*O-d* as the neat liquids.

at 1204 cm^{-1}. The VCD spectrum of (*R*)-1-phenylethanol [(*R*)-**2**] (Figure 2) also shows a VCD feature at 1204 cm^{-1} with other VCD bands at 1450, 1078, 1012, and 900 cm^{-1}. Since the infrared spectra of (*S*)-**3** (Figure 3), (*S*)-**4**, (*R*)-**5** (Figure 4), and (*R*)-**6**[26] also show similar absorption near 1200 cm^{-1} (Table III), the VCD associated with the absorption band near 1200 cm^{-1} appears to be characteristic of the phenylcarbinols **1–6**.

In these molecules, the PhC(OH)H group is a common structural feature, and if the VCD band at about 1200 cm^{-1} has major contributions from this group, it can be considered a probe group. Viewing the probe group with the fourth ligand behind it, a clockwise (CW) pattern of the probe group substituents (**15**) in the usual sequence rule priority, OH > Ph > H, designated as having a CW probe group chirality, correlates with a negative sign for the VCD band near 1200 cm^{-1}. For a counterclockwise (CCW) probe group chirality, this VCD band is positive (Table III).



CW probe group chirality

15

In order to justify this correlation, it must be shown that the major contribution to the VCD of the band at about 1200 cm^{-1} comes from within the probe group. Alternately, the infrared absorption of this band should arise from vibrational motions of one or more of the *C–OH, *C–Ph, and *C–H groups.

The possibility of a major contribution from the vibrational motions of the benzene ring to the band under consideration is excluded on the basis that the absorption band shape and its position remain unaffected on substitution by a chlorine atom in the para position of the benzene ring (compare Figures 1, 2, and 3). Similarly, major contributions from *C–O stretching are excluded on the basis that the infrared absorption due to this vibration is expected to be very strong and to be at about 1000 cm^{-1}. When the hydroxyl group in (±)-**2** is deuterated (**9**), the band near 1200 cm^{-1} in the infrared and Raman spectra is unaffected (see Figures 5 and 6), and the possibility[27] that this band is associated with a *C–O–H deformation motion is eliminated. When the methine hydrogen atom in (±)-**2** is replaced with a deuterium atom (**7**), however, the band near 1200 cm^{-1} disappears (see Figures 5 and 6) and a new band assignable to a *C–D deformation appears at 950 cm^{-1}. Thus the band under consideration has a contribution from *C–H deformation motion. In this region, however, vibrational bands are expected to have contributions from more than one internal coordinate, and others such as C–O and Ph–C stretches may have some contribution to the band of interest here. Such contributions cannot be deduced from the current experimental data, and therefore, the band is referred to simply as a *C–H deformation.

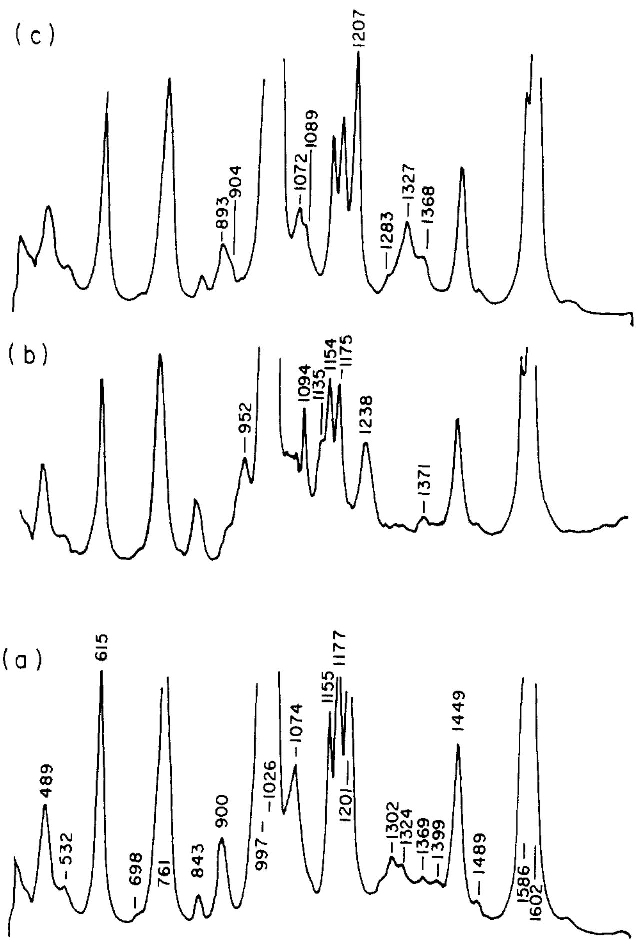


Figure 6. Multichannel Raman spectra for the compounds as labeled in Figure 5.

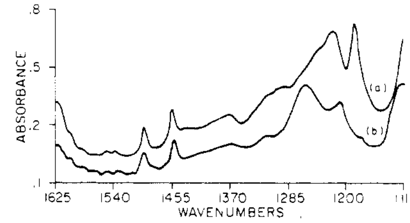


Figure 7. Fourier transform infrared absorption spectra of (a) (±)-mandelic acid [(±)-**5**] and (b) (±)-mandelic-*α-d* acid [(±)-**8**] as 0.5 M solutions in dimethyl-d_6 sulfoxide.

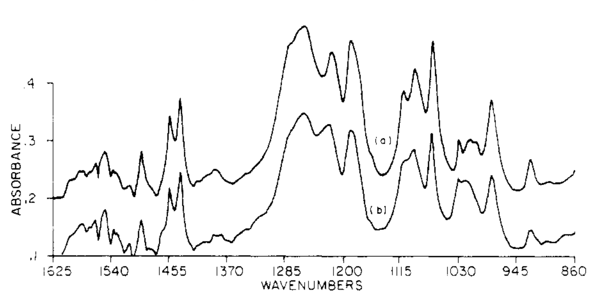


Figure 8. Fourier transform infrared absorption spectra of (a) methyl (*S*)-mandelate [(*S*)-**6**] and (b) methyl (*R*)-mandelate-*O-d* studied as 0.4 M solutions in carbon tetrachloride.

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[26] Figure 2 in ref 10.

[27] Varasanyi, C. "Assignments for Vibrational Spectra of Seven Hundred Benzene Derivatives"; John Wiley: New York, NY, 1974; p 65.

In the infrared spectra of mandelic acid (**5**) and its methyl ester (**6**), there are two absorption bands at about 1200 cm^{-1}, one slightly above and the other slightly below 1200 cm^{-1}. As seen in Figure 7, when the methine hydrogen atom in **5** is replaced by a deuterium atom (**8**), the band at 1187 cm^{-1} in the spectrum of **5** disappears. Hence this band (Figure 4) is considered to correspond to the band at about 1200 cm^{-1} in (*S*)-**1**, (*R*)-**2**, (*S*)-**3**, and (*S*)-**4**, and its sign correctly correlates (Table III) with the probe group chirality. As seen in Figure 8, the band at 1187 cm^{-1} in the infrared spectrum of methyl mandelate (**6**) is unaffected by deuteration of the hydroxyl group (**10**), and in analogy with the assignment made for (*R*)-**5**, the band at 1187 cm^{-1} in the VCD spectrum of (*R*)-**6** is assigned as corresponding to a *C–H deformation. The sign associated with the VCD of this band is also correlated (Table III) with the probe group chirality.

In the above analysis, it is implied that the phenylcarbinols exist in a similar preferred conformation. Compounds **1**–**4**, studied as neat liquids, have considerable intermolecular hydrogen bonding. For compounds **5** and **6**, studied in dimethyl sulfoxide and carbon tetrachloride, respectively, intramolecular hydrogen bonding is expected to dominate. The difference in hydrogen bonding for the two series of compounds, however, may not affect the VCD at 1200 cm^{-1} because the hydroxyl group is not involved in the vibrational motion as evidenced from the infrared spectra of **2**, **6**, **9**, and **10**. The assumption of a similar conformation for the molecules studied here has some support from conformational studies[28–30] on benzyl alcohol and α-alkylbenzyl alcohols.

Since the VCD band near 1200 cm^{-1} is assigned to a *C–H deformation, this deformation might constitute a certain combination of changes in the H–*C–Ph and H–*C–O angles. During this vibrational motion, charge redistribution from the benzene ring and from the lone pair of electrons on oxygen is probably involved in the magnetic dipole transition moment contribution to the VCD. The chirality of this charge redistribution could then be the basis for the correlation of the probe group chirality with the observed sign of the VCD band at about 1200 cm^{-1}.

Experimental Section

Melting points were taken in open capillary tubes and are corrected. Boiling points are also corrected. Rotatory powers at the sodium D line were measured with an Autopol III automatic polarimeter and a 1-dm sample tube. Proton magnetic resonance (^{1}H NMR) spectra were observed in chloroform-*d* with tetramethylsilane as an internal standard with a JEOL JNM-MH-100 or JNM-FX 90Q spectrometer, and all compounds characterized below had ^{1}H NMR spectra consistent with their assigned structures. The infrared spectra noted in Table II were observed with a Perkin-Elmer 710-B spectrometer. The high-performance liquid chromatography (HPLC) was done with a GOW-MAC Model 080-20 instrument fitted with a Partisil-10 ODS-3 column (0.46 × 25 cm) at a flow rate of 1 mL/min of methanol–water (1:1) as eluant. Electronic absorption (EA) spectra were measured with a Cary Model 14 spectrometer with matched 1-cm cells and the normal variable slit. Electronic circular dichroism (CD) spectra were obtained at 25–28 °C with a Cary Model 60 spectropolarimeter with a CD Model 6001 accessory. The sample cell was 1 cm, and the slit was programmed for a spectral band width of 1.5 nm. Cutoff was indicated when the dynode voltage reached 400 V. Vibrational circular dichroism (VCD) measurements were carried out on a FTIR-VCD spectrometer as described elsewhere.[31,32] Infrared absorption measurements, except those cited in Table II, were obtained with this same spectrometer. Raman spectra were observed with a multichannel Raman spectrometer assembled in our laboratory.[33] Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, TN.

(*S*)-Benzyl-α-*d* Alcohol [(*S*)-1]. Benzaldehyde-*1*-*d*[18] (**11**) was reduced with 3-pinanyl-9-BBN by the method of Midland, Greer, Tramontano, and Zderic.[14] The crude product (69%) showed a small impurity of isopinocampheol and was therefore purified via the acid phthalate to give pure (*S*)-**1** (53%): bp 105–106 °C (25 mmHg); d^{20}_{4} 1.05 [lit.[14] $[\alpha]^{25}_{D}$ +1.56 (neat), 88% ee].

(±)-Benzyl-α-*d* Alcohol [(±)-1]. Benzaldehyde in ether was reduced with lithium aluminum deuteride. Isolation and distillation gave pure (±)-**1** (88%): bp 109–111 °C (28 mmHg).

(*R*)-1-Phenylethanol [(*R*)-2] was an oil and had bp 107–109 °C (28 mmHg), d^{20}_{4} 1.01, $[\alpha]^{25}_{D}$ +41° (*c* 1.44, CH_3OH) [lit.[15] α_D +45.7° (neat, 1 dm), 100% ee].

(±)-1-(*p*-Chlorophenyl)ethanol [(±)-3]. *p*-Chloroacetophenone (100 g, 0.647 mmol) was added to an ice-chilled solution of sodium borohydride (12.1 g, 0.320 mol) in isopropyl alcohol (150 mL). The mixture was stirred for 30 min at 0 °C and then for 1 h at room temperature and finally poured into crushed ice (400 g) and concentrated hydrochloric acid (150 mL). The solution was washed with saturated sodium bicarbonate (2 × 50 mL) and saturated sodium chloride (2 × 50 mL). Evaporation of the dried ($MgSO_4$) ether solution gave the crude alcohol as a residue. Distillation gave pure (±)-**3** (90.2 g, 89%): bp 133–136 °C (20 mmHg) [lit.[19] bp 140–142 °C (31 mmHg)].

(*S*)-1-(*p*-Chlorophenyl)ethanol [(*S*)-3]. (*S*)-α-Phenylethylamine (42.0 g, 0.347 mol) was added with stirring to (±)-1-(*p*-chlorophenyl)ethyl acid phthalate (see below) (110 g, 0.361 mol) in boiling 95% ethanol (600 mL). On cooling, fine needles (101 g, 131%) were deposited. Five recrystallizations from 95% ethanol gave a pure salt (18.4 g, 24%) as fine, white needles: mp 143–145 °C; $[\alpha]^{25}_{D}$ +26° (*c* 1.09, CH_3OH), the specific rotation not changed on further recrystallization from 95% ethanol.

The salt was decomposed with 6 N hydrochloric acid (250 mL) and the acid phthalate ester collected by extraction into ether (3 × 50 mL). The ether solution was dried ($MgSO_4$), and evaporation gave the ester (13.0 g, 98%) as an oil: $[\alpha]^{25}_{D}$ +23° (*c* 0.48, CH_3OH). The oil (13.0 g, 42.7 mmol) was boiled with 30% sodium hydroxide for 1.5 h, and the cooled mixture was extracted with ether (3 × 30 mL). The ether solution was washed with saturated sodium chloride (2 × 20 mL) and dried ($MgSO_4$). After evaporation of the ether, distillation of the residue gave (*S*)-**3** (5.6 g, 84%): bp 133–136 °C (20 mmHg): d^{25}_{4} 1.16; $[\alpha]^{27}_{D}$ −47° (*c* 2.13, $(CH_3CH_2)_2O$) [lit.[16] +49.9° (*c* 2, $(CH_3CH_2)_2O$) for the enantiomer, 100% ee].

Hydrogenolysis of (*S*)-1-(*p*-Chlorophenyl)ethanol [(*S*)-3]. A mixture of (*S*)-**3** (1.00 g, 6.39 mmol), absolute ethanol (15 mL), potassium hydroxide (1.50 g) and 5% palladium on carbon (0.10 g) was stirred under an atmosphere of hydrogen (738 mmHg and 25 °C) until 1 molar equiv of hydrogen (161 mL) had reacted (3 h). The catalyst was removed by filtration, and the filtrate was evaporated. Saturated sodium chloride (15 mL) was added and the mixture extracted with ether (3 × 10 mL). The ether solution was dried ($MgSO_4$) and evaporated. The residue (0.70 g) was an oil and had $[\alpha]^{25}_{D}$ −40° (*c* 1.40, CH_3OH). A portion of the residue was subjected to HPLC analysis which showed two components with peak areas in a ratio of 49:1 with respective retention times of 3.5 and 9.0 min corresponding, respectively, to those of (±)-1-phenylethanol [(±)-**2**] and (±)-1-(*p*-chlorophenyl)ethanol [(±)-**3**].

(±)-1-(*p*-(Trifluoromethyl)phenyl)ethanol [(±-**4**] was prepared (92%) from *p*-(trifluoromethyl)acetophenone by reduction with sodium borohydride as outlined for the preparation (±)-**3** and had bp 112–114 °C (20 mmHg) [lit.[20] bp 106–107 °C (18 mmHg)].

(*S*)-1-(*p*-(Trifluoromethyl)phenyl)ethanol [(*S*)-**4**] was prepared by resolution of the acid phthalate ester of (±)-**4** (see below) with (*S*)-α-phenylethylamine as outlined for the resolution of (±)-1-(*p*-chlorophenyl)ethyl hydrogen phthalate. After six recrystallizations from isopropyl alcohol, the (*S*)-α-phenylethylamine salt of the acid phthalate ester of (*S*)-**4** (28%) had mp 148–149 °C; $[\alpha]^{25}_{D}$ +28° (*c* 1.18, CH_3OH). Decomposition of the salt as outlined above gave the ester (98%): mp 100–102 °C; $[\alpha]^{25}_{D}$ +21° (*c* 1.03, CH_3OH). Saponification of the ester gave (*S*)-**4**: bp 112–114 °C (20 mmHg); $[\alpha]^{25}_{D}$ −29° (*c* 1.69, CH_3OH).

Optical Purity of (*S*)-1-(*p*-(Trifluoromethyl)phenyl)ethanol [(*S*)-4]. (*S*)-α-Methoxy-α-(trifluoromethyl)phenylacetic acid chloride, bp 45–48 °C (0.5 mmHg), $[\alpha]^{23}_{D}$ −127° (*c* 1.55, CCl_4) [lit.[34] $[\alpha]^{24}_{D}$ +135.0° (*c* 5.17, CCl_4) for the *R* isomer] (0.056 g, 2.2 mmol), and (*S*)-**4** (0.028 g, 1.5 mmol) were mixed with carbon tetrachloride (5 drops) and dry pyridine (5 drops). The mixture was protected from water in the air and stirred at room temperature for 24 h. After isolation in the usual way,[34] the ^{1}H NMR spectrum of the oily reaction product showed two overlapped but distinct doublets at 1.59 and 1.64 ppm, each with $J = 6$ Hz, in an intensity of 95 to 5, respectively, assigned to methyl protons of the alcohol moiety of the diastereomeric esters. Other signals in this same

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intensity ratio, respectively, were 6.16 and 6.11 (q, $J = 6$ Hz, C-1 H) and 3.48 and 3.56 ppm (br s, CH_3O).

(*R*)- and (*S*)-Mandelic acid [(*R*)- and (*S*)-5] had mp 131–133 and 132–133 °C, respectively [lit.[17] mp 133 and 133 °C; $[\alpha]^{18}_D$ −153.5° (*c* 1.47, absolute C_2H_5OH) and $[\alpha]^{19}_D$ +151.5° (*c* 1.45, absolute C_2H_5OH) for (*R*)- and (*S*)-**5**, respectively].

Methyl (*R*)- and (*S*)-mandelate [(*R*)- and (*S*)-6] had mp 56–57 and 56–58 °C, respectively [lit.[17] mp 58 and 58 °C; $[\alpha]^{20}_D$ −177° (*c* 1.3, $CHCl_3$) and +175° (*c* 1.3, $CHCl_3$) for (*R*)- and (*S*)-**6**, respectively].

(±)-1-Phenylethanol-*1-d* [(±)-7] was obtained by reduction of acetophone in ether with lithium aluminum deuteride. Isolation and distillation gave (±)-**7** (91%) as a colorless oil: bp 100–102 °C (20 mmHg).

(±)-Mandelic-*α-d* acid [(±)-8] was prepared by reduction of benzoylformic acid with sodium borodeuteride by the same procedure as described for the reduction of *p*-chloroacetophone with sodium borohydride. The acid (±)-**8** was obtained (84%) as a white solid: mp 114–117 °C.

(±)-1-Phenylethanol-*O-d* [(±)-9]. (±)-1-Phenylethanol [(±)-**2**] (5.0 g, 8.2 mmol) was added to deuterium oxide (7.0 g, 0.35 mol), and the heterogeneous mixture was shaken for 18 h. The alcohol was extracted into ether (2 × 25 mL), and the ether solution was dried ($MgSO_4$). Evaporation of the ether and distillation of the residue gave (±)-**9** as a colorless oil: bp 98–102 °C (20 mmHg); ^1H NMR δ 1.48 (d, 3, $J = 8$ Hz, CH_3), 4.88 (q, 1, $J = 8$ Hz, $CHCH_3$), 7.40 (m, 5, aromatic H).

Methyl (*R*)-mandelate-*O-d* [(*R*)-10] was prepared from methyl (*R*)-mandelate by deuterium exchange in deuterium oxide–methanol-*O-d*. Lyophilization of the mixture gave (*R*)-**10** as a white solid: mp 54–56 °C.

Benzaldehyde-*1-d* (11). To a stirred solution of benzil (13.9 g, 66.1 mmol) in *p*-dioxane (30 mL) was added deuterium oxide (14.4 g, 0.719 mol) and then potassium cyanide (4.68 g, 71.9 mmol) in five portions over 0.5 h. The mixture was stirred for another 0.5 h and then diluted with water (120 mL). The mixture was extracted with ether (3 × 50 mL) and the ether solution washed with saturated sodium bicarbonate (2 × 50 mL) and saturated sodium chloride (2 × 50 mL). After evaporation of the dried ($MgSO_4$) ether solution, distillation gave pure **11** (4.32 g, 61%) as an oil: bp 76–78 °C (22 mmHg) [lit.[18] bp 84–86 °C (30 mmHg)].

(±)-1-(*p*-Chlorophenyl)ethyl Acid Phthalate. A mixture of (±)-1-(*p*-chlorophenyl)ethanol [(±)-**3**] (85.1 g, 0.543 mol), phthalic anhydride (80.5 g, 0.544 mol), and pyridine (86.0 g, 1.09 mol) was stirred overnight at room temperature and then 2 h at 100 °C. The cooled mixture was poured over crushed ice (100 g) and concentrated hydrochloric acid (90 mL), and the mixture was extracted with chloroform (3 × 100 mL). The chloroform solution was evaporated. The residue was neutralized with an excess of saturated sodium carbonate, and the mixture was extracted with ether (2 × 30 mL). The aqueous solution was made acidic (pH 2) by the addition of dilute hydrochloric acid, and the mixture was extracted with ether (3 × 100 mL). The ether solution was dried ($MgSO_4$) and evaporated. Recrystallization of the residue from acetic acid–water (85:15) gave the acid phthalate ester (111 g, 67%): mp 107–108 °C.

Anal. Calcd for $C_{16}H_{13}ClO_4$: C, 63.06; H, 4.30. Found: C, 62.89; H, 4.26.

(±)-1-(*p*-(Trifluoromethyl)phenyl)ethyl acid phthalate was prepared (87%) from (±)-1-(*p*-(trifluoromethyl)phenyl)ethanol [(±)-**4**] by reaction with phthalic anhydride as outlined above for reaction of (±)-**3** with phthalic anhydride, was recrystallized from acetic acid–water (4:1) and had mp 113–114 °C.

Anal. Calcd for $C_{17}H_{13}F_3O_4$: C, 60.36; H, 3.87. Found: C, 60.33; H, 3.86.

***p*-Nitrobenzoate Derivatives.** *p*-Nitrobenzoyl chloride (1.00 g, 5.39 mmol), freshly recrystallized from petroleum ether (bp 35–38 °C), was slowly added with cooling to a stirred solution of the alcohol (4.9 mmol) in pyridine (2.50 g). Stirring was continued for an additional 24 h at room temperature, and the solution was diluted with ether (50 mL). The ether solution was extracted with 2 N hydrochloric acid (3 × 10 mL), saturated sodium bicarbonate (10 mL), and finally saturated sodium chloride (3 × 10 mL). The ether solution was dried ($MgSO_4$) and evaporated. The residue of crude benzoate ester was 85–98% of the theoretical and, when a solid at room temperature, was recrystallized from ethanol. Physical properties are given in Table II.

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Methoxychlorocarbene. Matrix Spectroscopy and Photochemistry

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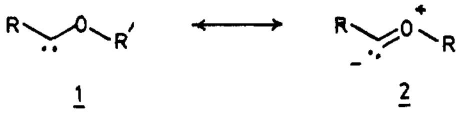
Abstract: Irradiation of 3-chloro-3-methoxydiazirine matrix isolated in argon or nitrogen at 10 K gives methoxychlorocarbene. The carbene was observed by IR and UV spectroscopy. Deuterium and ^{18}O labeling indicated significant C–O double bond character in the carbene, which was exhibited in an intense IR absorption at ca. 1300 cm^{-1}. The time evolution and wavelength dependence of the IR bands indicate two geometric isomers for the carbene, with distinct IR absorptions. The *cis*-carbene shows a significantly lower energy C–Cl stretch than the trans, consistent with an anomeric interaction. Irradiation of the carbene gives acetyl chloride, ketene, and HCl in argon matrices. In nitrogen, small amounts of CO and methylchloride are also observed. Several mechanisms are proposed to explain the photochemical results.

Despite extensive investigations into the structure, reactivity, and spectroscopy of carbenes,[1,2] there is a paucity of experimental information on oxycarbenes (e.g., **1**). Haloalkoxycarbenes were first postulated by Hine in 1953 as intermediates in the reactions of dichlorocarbene with alkoxides.[3] Since that time, oxycarbenes have been suggested as intermediates in thermolyses of norbornadienone ketals[4,5] and ester tosylhydrazone salts.[6,7] These



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