(*c* 3.48, benzene) the product, (*S*)-(+)-**7**, had specific rotation given in the text.

Reaction of 1 with 7.—A solution of 998.8 mg (5.89 mmol) of **1** in 5 ml of dry pyridine was added rapidly, with magnetic stirring to 990.6 mg (5.88 mmol) of **7** cooled to 0° by means of an ice bath. Reaction, as gauged by the appearance of pyridine hydrochloride, was immediate. The reaction mixture, protected from moisture, was stirred for 2.5 hr, while the temperature climbed from 0 to 25°. The solution was poured over an equal volume of ice and extracted with ether (five 8-ml portions), which was then washed repeatedly with 1 *N* sulfuric acid until all pyridine had been removed, and once with saturated sodium chloride solution. The ether solution was dried, then rotary evaporated, leaving 1418.1 mg (81%)[21] of the product as an oil which did not freeze above −20°. Glpc showed two components, one at 8.4 min (48.6%) and one at 9.8 min (51.4%). Distillation gave an analytically pure mixture, slightly enriched in A, the lower boiling isomer (ratio of A to B 51:49), bp 88–91° (0.2 mm); *m/e* 300; ir (carbon tetrachloride) 2970, 2275, 1730, 1605, 1165 cm^{-1}. The pmr spectrum (carbon tetrachloride, internal TMS) clearly showed two sets of absorptions, the relative isomer distributions from which corresponded to within 1% of the ratio found with glpc. Isomer A: δ 7.27 (br s, 5 H), 5.05 (s, 1 H), 3.69 (q, J = 7.3 Hz, 1 H), 1.48 (d, J = 7.3 Hz, 3 H), 1.13 (s, 9 H), 0.92 (s, 9 H); Isomer B: δ 7.27 (br s, 5 H), 5.08 (s, 1 H), 3.68 (q, J = 7.3 Hz, 1 H), 1.48 (d, J = 7.3 Hz, 3 H), 1.21 (s, 9 H), 0.79 (s, 9 H).

Anal. Calcd for $C_{20}H_{28}O_2$: C, 79.95; H, 9.39. Found: C, 79.76; H, 9.41.

When the reaction was carried out with the resolved materials, the product, isolated in 86%[21] yield, gave an ir spectrum virtually superimposable on that of the diastereomer mixture (*vide supra*). This material, predominantly (*RS*)-(+)-**8**, did solidify to a glass at 0°, and remelted at ~30°; its specific rotation is given in the text. The pmr spectrum of the product was identical with that of B above, with *ca.* 5% of A discernible. Glpc showed a ratio of 4.0:96.0 (A:B). A 198-mg sample of racemic ester mixture was dissolved in 2 ml of dry pyridine and allowed to stand for 11.5 hr at ambient temperature. Work-up as above and then glpc analysis showed that the constitution of the mixture had changed by less than 2%.

Registry No.—**1**, 22688-43-3; **1** phthalic half ester, 33122-22-4; **1** phthalic half ester brucine salt, 33069-02-2; **6**, 7782-24-3; **6** strychnine salt, 33069-04-4; **7**, 25145-43-1; *R*,*R*-**8**, 33069-06-6; *S*,*S*-**8**, 33069-07-7; (+)-*R*,*S*-**8**, 33069-08-8; *S*,*R*-**8**, 33122-23-5.

Acknowledgments.—We wish to thank Mr. Eugene R. Kennedy for preparing compounds **3** and **4** (Table I) and the University of Cincinnati Graduate School for partial support in the form of a Summer Research Fellowship to R. S. M. Acknowledgment is further made to the Donors of the Petroleum Research Fund administered by the American Chemical Society for partial support of this work.

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[21] It is significant to note that although isolated yields are somewhat less than quantitative, glpc analysis of the crude product mixtures showed unreacted **1** as the only contaminant.

Magnetic Circular Dichroism Investigations of Some Conjugated Olefins[1,2]

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The magnetic circular dichroism (MCD) curves of 12 conjugated dienes are reported. The series studied includes both acyclic and cyclic *s-cis*- and *s-trans*-dienes as well as compounds having a large range in skew angle values. From the lack of variation in the signs and magnitudes of the B/D values measured for the dienes studied, it is concluded that MCD, in the 200–300-nm region, has no distinct advantage over absorption spectroscopy for the structural identification of different diene systems. 1,3,5-Cycloheptatriene exhibits a more complex MCD spectrum than anticipated.

Magnetic circular dichroism (MCD) and magnetic optical rotatory dispersion (MORD) have been useful tools in the investigation of molecular structure[1] and in some cases have been found to be more sensitive to molecular structrual differences than either CD or ORD.[5] MCD has also been used to clarify spectroscopic assignments, detect hidden transitions, and characterize the symmetry and angular momentum properties of molecules in their ground and excited states.[6] The most important advantage of MCD is that it can be applied to optically inactive or racemic material.

A resurgence of interest during the past several years is clearly in evidence.[1] The impetus for this renewed interest comes primarily from Buckingham and Stephens' theoretical treatment of magnetic optical activity within absorption bands.[6a] The magnetic molar ellipticity, $[\theta]_M$, associated with an isolated electronic transition $a \rightarrow j$, can be expressed by eq 1.[6b] In this

$$[\theta_{(a\rightarrow j)}]_M = -21.3458\,\{f_1 A_{(a\rightarrow j)} + f_2[B_{(a\rightarrow j)} + C_{(a\rightarrow j)}/kT]\} \quad (1)$$

equation, the B term results from the mixing of energy levels by the magnetic field and is present for all molecules. The A and C terms result from Zeeman splitting of degenerate levels by the external field, and nonzero values for these magnetic rotational strengths will be oberved only for highly symmetrical molecules. The B and C terms are described by the same shape function, f_2, and have the bell shape characteristic of an absorption band. The curve observed for the A term, described by f_1, is the resultant of two oppositely

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[1] Part XVI in the series Magnetic Circular Dichroism Studies. For part XV, see C. Djerassi, E. Bunnenberg, and D. L. Elder, *Pure Appl. Chem.*, **25**, 57 (1971), a review of the applications of MCD in organic chemistry.

[2] This work was supported in part by the National Institutes of Arthritis and Metabolic Diseases, U. S. Public Health Service (Grant No. AM-00709 to W. G. D.), the National Institutes of Health (Grant No. AM 12758 to C. D.), and the Stanford University Center for Materials Sciences.

[3] National Institutes of Health Predoctoral Fellow, 1968–1971.

[4] National Science Foundation Predoctoral Fellow, 1967–1971.

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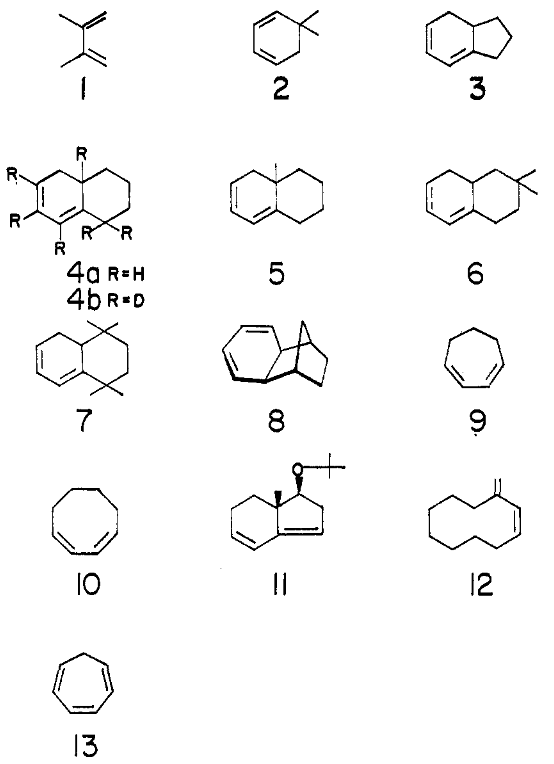

Figure 1.—Structures of the olefins investigated.

TABLE I

ABSORPTION AND MCD SPECTRA OF CONJUGATED OLEFINS IN HEXANE

Compd	Absorption[a] λ, nm (10^{-3} ε)	MCD[b,c,d] $λ_0$, nm ($10^3[\theta]_M$)	Γ, nm	B/D × 10^5
1	228 (10)	215 (neg)[e]		
2	258 (6.1)	256 (−83)	37	4.8
3	268 (4.9)	270 (−58)	40	3.3
4a	267 (6.8)	270 (−66)	29	2.4
4b	267 (6.6)	267 (−62)	38	3.4
5	264 (6.5)	264 (−51)	34	2.6
	274 (sh)	275 (−47)		
6	267 (6.4)	270 (−37)	41	1.9
7	269 (5.2)	270 (−47)	40	2.8
	278 (5.0)	282 (−40)		
8[f]	268 (4.3)	263 (−38)	47	3.4
	279 (4.0)	271 (−47)		
	288 (sh)	283 (−39)		
		294 (−19)		
9	246 (7.5)	255 (−47)	30	2.2
10	228 (5.5)	220 (neg)[e]		
11[g]	236 (15.0)	235 (−96)	28	2.1
	242 (15.0)	243 (−104)		
12[h]	214 (7.0)	210 (neg)[e]		
13	265 (4.2)	251 (−153)	35[i]	9.9[j]
		284 (+5)		
		302 (−10)		

[a] Only well-defined shoulders are given. [b] $[\theta]_M$ is molar magnetic ellipticity in deg cm^2 dmol^{-1} G^{-1}. [c] Γ is the full width of the MCD at one-half maximum height. [d] The ratio of the magnetic rotational strength to the dipole strength was computed by the moment analysis procedure outlined in ref 7d and 7f. $B/D = -3.25 \int([\theta]_M/\nu)d\nu / \int(\epsilon/\nu)d\nu$ in β_M/cm^{-1} and β_M is the Bohr magneton. [e] $[\theta]_M$ is negative but a clearly defined maximum was not reached at the wavelength indicated. [f] Supplied by M. S. Kellogg. [g] Supplied by T. J. Dietsche. [h] Supplied by C. Suter. [i] Half band width of the 251 nm MCD band. [j] See comments in text.

signed bell-shaped components which are symmetrically located on either side of the absorption band maximum. Thus, in the general case, the MCD curve observed for an isolated electronic transition can be expected to have a complex envelope.

Much attention has been directed toward the evaluation of the A and C terms, since these magnetic rotational strengths provide extremely useful spectroscopic information about the excited and ground states for both organic and inorganic systems having the appropriate symmetry.[6b,7f] However, accurate values for these two terms are difficult to extract from experimental curves when several transitions are closely spaced. Furthermore, the curve resulting from two overlapping oppositely signed B terms can closely resemble the curve from an A term, a situation which may lead to incorrect transition assignments.

On the other hand, values for the ubiquitous B terms have been determined only for a limited number of organic compounds and then only in the course of extracting A values. A general interpretation of the MCD spectra of compounds which are of such low symmetry as to show only B terms is difficult since, in principle, the entire manifold of states must be considered. Consequently, interpretations of the MCD spectra of the vast majority of organic compounds is likely to be empirical in nature. In the present communication we report the MCD spectra and the B/D values (D = dipole strength) for a number of different conjugated dienes. The series studied includes both acyclic and cyclic *s-cis-* and *s-trans-*dienes and includes compounds having a large range in skew angle values and molecular environments. These latter features are of interest since the ORD[8a,b] of chiral dienes is known to be unusually sensitive to structural parameters.

In the simple two-state case where a nondegenerate ground state *a* is coupled with only two nondegenerate excited states *j* and *k*, theory[6] predicts that the magnetic rotational strengths associated with the transitions $a \rightarrow j$ and $a \rightarrow k$ will be of equal magnitude but of opposite sign. The sign of the B terms depends on the polarization of the transitions and, hence, cannot be determined because of the arbitrary orientation of the molecule in the symmetry axis and the Hermitian character of the magnetic and electric momentum operators.[9,10a] The expression for the B term involves the scalar triple product of the two electric dipole moments and the connecting magnetic dipole moment as given in the simplified expression,[10a] eq 2,

$$B_{(a \rightarrow j)} = I_m \sum_{k \neq j} \frac{\boldsymbol{\mu}_{jk} \cdot \mathbf{m}_{aj} \cdot \mathbf{m}_{ka}}{\nu_{kj}} \qquad (2)$$

where **m** and **μ** are the electric and magnetic dipole transition moments, respectively, and ν_{kj} is the energy

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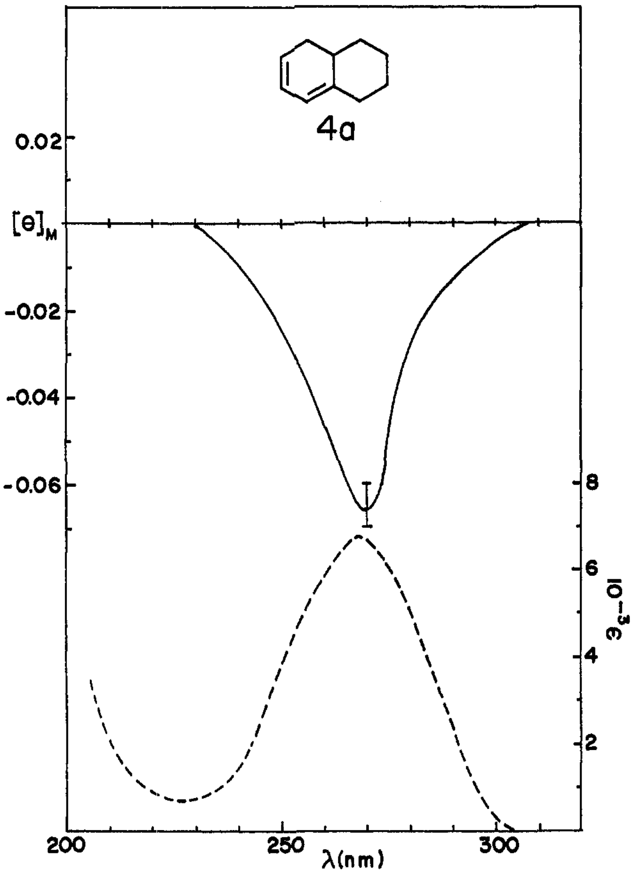

Figure 2.—Absorption (------) and MCD (——) spectra of 1,2,3,4,8,9-hexahydronaphthalene (**4a**) in hexane.

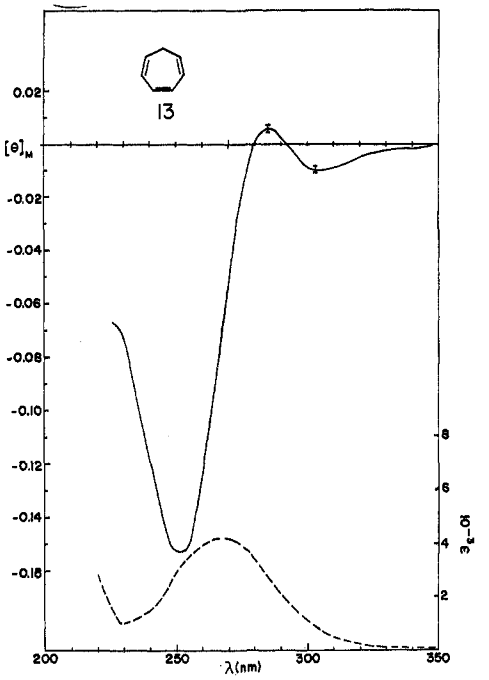

Figure 3.—Absorption (------) and MCD (——) spectra of 1,3,5-cycloheptatriene (**13**) in hexane.

difference between the states *j* and *k*. The dipole strength for the nondegenerate transition $a \rightarrow j$ is given by eq 3. Equations 2 and 3 illustrate one of the

$$D_{(a \rightarrow j)} = |m_{(a \rightarrow j)}|^2 \qquad (3)$$

analytical applications of MCD; namely, that a weak absorption band may lead to a strong MCD band. Several examples can be found in the MCD spectra of purine derivatives[5] and, more dramatically, in the MCD associated with the Q_0^x and Q_0^y absorption bands of chlorin derivatives.[10b]

The compounds studied are shown in Figure 1 and their absorption and MCD properties are given in Table I. The MCD and absorption spectra of **4a** (Figure 2) are typical of the dienes studied, except for compounds **1**, **10**, and **12**, for which a negative MCD was measured although a clear maximum was not detected at wavelengths corresponding to their absorption maxima. For the remaining dienes only the lowest energy B term is observed since the higher energy B term(s) was not accessible with our instrument. The position of the observed λ_0 of the maximum molar ellipticity, $[\theta]_M$, of these dienes is in the vicinity of their absorption maxima, λ_{max}, as predicted by theory for allowed transitions. In addition, those compounds which exhibit fine structure in their absorption spectra also show similar fine structure in the MCD curves. Indeed, in most cases, the MCD is virtually a mirror image of the absorption spectra. The lack of a clearly defined maximum in the MCD spectra of the compounds having either a large degree of conformational mobility, **1**, or sterically imposed large skew angles,[11] **10** and **12**, may be attributed to the low signal-to-noise ratios prevailing at lower wavelengths. On the basis of the lack of variation in the signs of the B terms observed for the *s-cis-* and *s-trans-*dienes (*e.g.*, **4a** and **11**, respectively) as well as the lack of variation in the ratio B/D for the dienes studied, it appears that MCD does not, in fact, exhibit the conformational sensitivity. Furthermore, examination of the values of B/D reported for several organic systems (Table II) shows that this ratio cannot be used to characterize a particular chromophore, since factors such as the energy separation between states, the relative orientation of transition moments, the vagaries attending complex mixing of more than two excited states, and the particular data analysis procedure used must also be considered.

TABLE II

B/D VALUES REPORTED FOR SOME ORGANIC COMPOUNDS

Compd	Transition (λ_{max}, nm)	B/D × 10^5 (β_M/cm^{-1})	Ref
Dienes	230–290	1.9–4.8	
Annulenes	330–370	4.8–9.1	7e
Coronene	303	0.396	7f
Triphenylene	255	−2.32	7f
Zn Hematoporphyrin	578 (Q_0)	−134	7a
	413 (Soret)	3.47	
Coproporphyrin II	625 (Q_0^x)	216	7a
tetramethyl ester	526 (Q_0^y)	−95.9	

As the data in Table 1 and Figure 3 indicate, the MCD of cycloheptatriene does not conform to any of the previous generalizations. The experimental curve in Figure 3 can be visualized as the sum of overlapping oppositely signed B terms. Nmr evidence[12] would seem to render the rationalization of a cycloheptatriene–norcaradiene equilibrium untenable. Among

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the other explanations which might be considered are (1) vibrational effects; (2) separate contributions from planar and nonplanar conformers;[12] (3) mixing of a singlet state with a nearby triplet state; and (4) complex mixing with low-lying singlet states. Clearly, further work is required; however, some support for low-lying states can be found in the electron impact excitation spectrum of cycloheptatriene recently reported by Oosterhoff.[14] It should be noted that the ratio $B/D = 9.9 \times 10^{-5}\ \beta_M/\mathrm{cm}^{-1}$, although distinctly larger than the mean of the diene values, was determined by moment analysis[7f] and has significance only if the complex MCD is of vibrational rather than electronic origin.

In conclusion, our results support the current theoretical treatment of the Faraday effect and provide additional spectroscopic evidence for the prediction[11] of but a single electronic transition in the 200–300 nm region of conjugated dienes. Furthermore, these results provide the basis, and indeed the impetus, for further measurements in the vacuum ultraviolet. Although MCD in the 200–300 nm region has no distinct advantage over absorption spectroscopy for the structural identification of different diene systems, further work in this region on triene systems is definitely warranted.

Experimental Section

The synthesis and photochemical transformations of these compounds will be described in a future publication.

MCD measurements were made using a Japan Spectroscopic Company spectropolarimeter (Durrum-JASCO Model ORD/UV/CD-5) modified to accept a Lockheed Palo Alto Research Laboratories superconducting magnet (Model OSCM-103). The directions of the light beam and the positive sense of the magnetic field are coincident. All measurements were made at 21° in a magnetic field of 49.5 kG. The solvent was Spectrograde hexane.

Registry No.—**1**, 513-81-5; **2**, 33482-80-3; **3**, 33482-81-4; **4a**, 13376-06-2; **4b**, 33482-83-6; **5**, 33482-84-7; **6**, 33482-85-8; **7**, 33482-86-9; **8**, 33482-87-0; **9**, 4054-38-0; **10**, 3806-59-5; **11**, 33495-82-8; **12**, 31351-58-3; **13**, 544-25-2.

Acknowledgment.—The excellent technical assistance provided by Ruth Records, Gordon H. Scott, and Angus M. Babcock is gratefully appreciated.

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Stereospecific Introduction of Functionalized Angular Methyl Groups *via* the Claisen Rearrangement. The Octalin and Hydrindenyl Ring Systems[1,2]

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The one-step Claisen rearrangement using ethyl vinyl ether, *N*,*N*-dimethylacetamide dimethyl acetal, or triethyl orthoacetate provides a useful method for the preparation of octalin systems with functionalized angular methyl groups from octalols. This method fails with the hydrindenyl ring system. However, preparation and purification of vinyl ethers followed by thermolysis lead to functionalized methyl groups in both ring systems. The use of decalin as solvent in the thermolysis increases the amount of Claisen product in the hydrindenyl system. When the temperature is lowered, the rate of rearrangement is decreased and the amount of elimination increased.

In the synthesis of polycyclic sesqui- and diterpenes, the need often has arisen for a general stereospecific preparation of fused ring systems with functionalized angular methyl groups. Such a group has usually been introduced into the ring systems by a conjugated addition of hydrocyanic acid[3] or by functionalizing[4] an already present angular group. Previous studies[5] in this laboratory with regard to the stereospecific introduction of an angular methyl group *via* cyclopropanation of an allylic alcohol called attention to this latter system as a potential starting point for other stereospecific syntheses. Indeed, such a system has been utilized by conversion to a vinyl ether followed by a Claisen rearrangement to a γ,δ-unsaturated aldehyde.[6] The reports in the recent literature[7–9] of three different one-step methods (eq 1–3) for bringing about this conversion made this an attractive pathway to evaluate.

These three reaction sequences were studied using the allylic alcohols **1** and **4**, ring systems which typify those found in natural products. It wasf ound that, when the one-step method using ethyl vinyl ether (eq 1) with the recommended trace of phosphoric acid as a catalyst was employed, the sole products of the reac-

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[2] In this paper the term hydrindenyl is used to describe the tetrahydroindan system represented by structures such as **4** and **5**.

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