

Table I. Specific Rotations of Some Alkyl Benzyl Sulfoxides in Ethanol and Chloroform

Alkyl group	In ethanol		In chloroform	
	Percamphoric acid oxidn., ^a deg.	Grignard synthesis, ^b deg.	Percamphoric acid oxidn., ^a deg.	Grignard synthesis, ^b deg.
Methyl ^c	+1.0 (1.0)	+96	-0.5 (0.9)	-55
Ethyl	+1.2 (2.5)	+47	-2.9 (3.0)	-97
<i>n</i> -Butyl	+0.7 (4.4)	+16	-1.8 (1.7)	-105
Isopropyl	+5.3 (4.5)	+119	+0.6 (20)	+3
<i>t</i> -Butyl	+12.0 (4.3)	+281	+10.3 (4.3)	+240

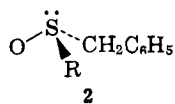
^a With the exception of the methyl compound, the data are taken from ref. 2. Values in parentheses are *maximum* per cent optical purities calculated on the basis of the rotations listed in the adjoining column. ^b Reaction of alkylmagnesium halide and I. ^c Present work, following the procedure reported in ref. 2.

suggested² on the basis of a proposed transition state that the direction of asymmetric synthesis follows a general pattern which can be summarized as follows: oxidation of a sulfide A-S-B with (+)-monopercamphoric acid gives a preponderance of the enantiomer shown in stereoformula 1 when A is bulkier than B.



Although this generalization correctly predicted the absolute configurations of alkyl phenyl sulfoxides,⁴ we now wish to report that it breaks down in the case of alkyl benzyl sulfoxides and thus may not be used as a general scheme for the assignment of absolute configurations to sulfoxides.

Reaction of phenylmethanesulfinyl chloride (C₆H₅-CH₂SOCl) with *l*-menthol followed by fractional crystallization of the reaction mixture afforded a diastereomer (I) of *l*-menthyl phenylmethanesulfinate, [α]_D +105° (chloroform). Reaction of I with *p*-tolylmagnesium bromide gave benzyl *p*-tolyl sulfoxide (II), [α]_D +228° (acetone), 91% optically pure based on the highest reported rotation.⁵ The absolute configuration of II is (*R*),^{4,5} corresponding to stereoformula 2, and since the Grignard reaction proceeds with inversion of configuration,^{4,6} it follows that ester I has the (*R*) configuration at sulfur.⁷ Reaction of a variety of branched and unbranched alkylmagnesium halides with I gave the compounds listed in Table I, all of which must have the configuration shown in stereoformula 2.



R = alkyl or *p*-tolyl

The rotational signs of the sulfoxides derived from I agree with the signs of the sulfoxides obtained by (+)-percamphoric acid oxidation of the corresponding sulfides (Table I). Therefore the predominant enantiomers produced in the asymmetric oxidation also have configuration 2. It follows that while the configurational assignments² based on the proposed transition state are correct in the cases of isopropyl benzyl and *t*-butyl benzyl sulfoxides, they are incorrect in the cases of *n*-alkyl benzyl sulfoxides (and, by extension, methyl benzyl sulfoxide) since the benzyl group is judged to be bulkier than *n*-alkyl groups.²

The stereospecificities of the asymmetric oxidations

(5) C. J. M. Stirling, *J. Chem. Soc.*, 5741 (1963).

(6) K. K. Andersen, *J. Org. Chem.*, 29, 1953 (1964).

(7) For configurational nomenclature, see ref. 4, footnote 10.

are extremely low. Quantitative comparisons are rendered suspect by inconsistencies in the optical yields as measured in ethanol and chloroform (Table I); these discrepancies are most likely due to inaccuracies in the small rotations observed in the asymmetric oxidations.² We therefore refrain from rationalization of our findings at this time.

A detailed study of this and related asymmetric oxidations is now under way. We shall report separately on the optical rotatory dispersion (including solvent effects) of alkyl benzyl sulfoxides.

(8) N.I.H. Predoctoral Fellow, 1964-1965.

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Circular Dichroism of Copper(II) Complexes with Optically Active Amino Acids

Sir:

Pfeiffer and Christeleit¹ have reported the usefulness of optical rotatory dispersion (ORD) of bis(optically active amino acid)copper(II) complexes as a tool in determining the configurations of the amino acids. The copper(II) complex of an L-amino acid shows a negative Cotton effect in the region of the visible *d* → *d* absorption band, and the complex of a D-amino acid a positive Cotton effect. The present communication reports a circular dichroism (CD) study of the complexes [Cu(am)₂] in aqueous solutions (am = L- and D-alanine, L-serine, L-valine, L-threonine, L-allo-threonine, L-proline, and L-hydroxyproline). The CD curves in the region from 1000 to 400 mμ were obtained on a Shimadzu spectrophotometer with CD attachment using 0.025 M, 0.05 M, or saturated solutions of those complexes in a 1-cm. cell. The copper(II) complexes employed were prepared from copper(II) hydroxide by the modified method of Abderhalden and Schnitzler.²

As might have been expected from recent CD studies by other workers^{3,4} the split components of the *d* → *d* transition were clearly separated. The CD curve of [Cu(L-ala)₂] shows a small positive band at about 730 mμ and two negative bands at 630 and 565 mμ (Figure 1). The curve of [Cu(L-ser)₂] is similar to that of [Cu(L-ala)₂] on the whole, namely, a small positive peak at about 730 mμ, a negative band at 595 mμ, and a negative shoulder at about 640 mμ. However, another small

(1) P. Pfeiffer and W. Christeleit, *Z. physiol. Chem.*, 245, 197 (1937).

(2) E. Abderhalden and E. Schnitzler, *ibid.*, 163, 94 (1927).

(3) B. E. Douglas, R. A. Haines, and J. G. Brushmiller, *Inorg. Chem.*, 2, 1194 (1963).

(4) R. D. Gillard, *J. Inorg. Nucl. Chem.*, 26, 1455 (1964).

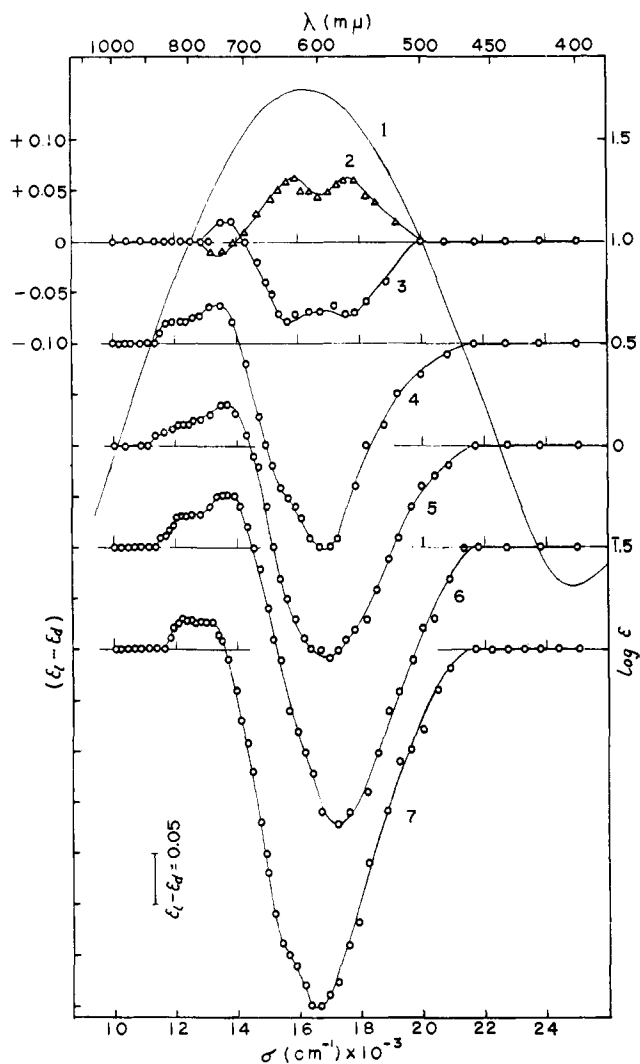


Figure 1. Absorption curve of (1) $[\text{Cu}(\text{L-ala})_2]$ and circular dichroism curves of (2) $[\text{Cu}(\text{D-ala})_2]$, (3) $[\text{Cu}(\text{L-ala})_2]$, (4) $[\text{Cu}(\text{L-ser})_2]$, (5) $[\text{Cu}(\text{L-thr})_2] \cdot \text{H}_2\text{O}$, (6) $[\text{Cu}(\text{L-val})_2] \cdot \text{H}_2\text{O}$, and (7) $[\text{Cu}(\text{L-allothr})_2] \cdot \text{H}_2\text{O}$ in aqueous solutions.

positive shoulder is observed at the longer wave length side (about $830 \text{ m}\mu$) of the positive peak. Similar trends are also observed in the curves of $[\text{Cu}(\text{L-thr})_2]$, $[\text{Cu}(\text{L-val})_2]$, and $[\text{Cu}(\text{L-allothr})_2]$. From Figure 1 it seems likely that the observed broad negative band of $[\text{Cu}(\text{L-thr})_2]$ or $[\text{Cu}(\text{L-val})_2]$ is caused by the superposition of two negative CD bands.

From these results it is concluded that the complex $[\text{Cu}(\text{L-am})_2]$ shows four CD components of the $d \rightarrow d$ transition which are related to the magnetic dipole allowed transitions under approximately C_{2h} symmetry, and that the L-configuration of the amino acid determines the signs of these CD components, namely, (+), (+), (-), and (-) from longer to shorter wave lengths. The single ORD inversion observed by Pfeiffer¹ is to be a superposition of four Cotton effects. In this point the present CD method appears to be preferable and more useful.

The CD curves of $[\text{Cu}(\text{L-prol})_2]$ and $[\text{Cu}(\text{L-hydprol})_2]$ show considerable difference from the other curves (Figure 2). In the former, this can be attributed to the stereospecific formation of a preferred asymmetric configuration about the nitrogen atom of the proline. Construction of the molecular models of complexes

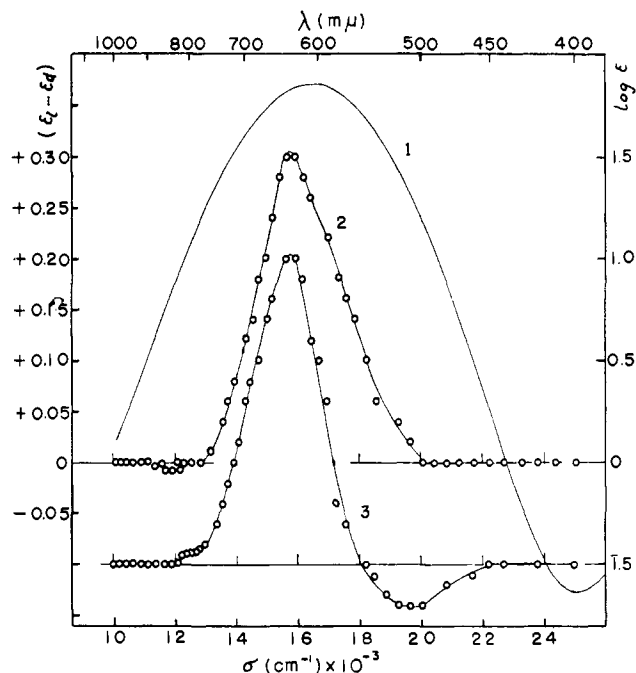


Figure 2. Absorption curve of (1) $[\text{Cu}(\text{L-prol})_2] \cdot 2\text{H}_2\text{O}$ and circular dichroism curves of (2) $[\text{Cu}(\text{L-hydprol})_2] \cdot 3\text{H}_2\text{O}$ and (3) $[\text{Cu}(\text{L-prol})_2] \cdot 2\text{H}_2\text{O}$ in aqueous solutions.

shows that the stereospecificity is perfect and that the nitrogen atom of the coordinated L-proline takes a forced asymmetric configuration and that of the coordinated D-proline the enantiomorphous configuration. This is also supported by X-ray analysis of the $[\text{Cu}(\text{L-prol})(\text{D-prol})] \cdot 2\text{H}_2\text{O}$ crystal.⁵ The vicinal effect from the activated nitrogen atom will be more effective than that from the asymmetric carbon atom, since the nitrogen atom directly attaches to the copper atom but the carbon atom indirectly. The former vicinal effect surpasses the latter and the difference between Figures 1 and 2 is caused.

(5) A. M. Mathieson and H. K. Welsh, *Acta Cryst.*, **5**, 599 (1952).

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Generation of Methylene by Photolysis of Hydrocarbons

Sir:

Methylene sufficiently active to insert into saturated carbon-hydrogen bonds is usually generated by photolysis of ketene¹ and by photolysis² or pyrolysis³ of diazomethane. Photolysis of diazine⁴ has also been found to yield a methylene having insertion activity. We now wish to report the generation of methylene by photolysis of hydrocarbons containing a cyclopropyl group adjacent to an aromatic ring. The resulting methylene in hydrocarbon solution exhibits the same indiscriminate insertion into alkane carbon-hydrogen

(1) H. M. Frey and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **79**, 6373 (1957).

(2) W. von E. Doering, R. G. Buttery, R. G. Laughlin, and N. Chaudhuri, *ibid.*, **78**, 3224 (1956).

(3) (a) B. S. Rabinovitch and D. W. Setser, *ibid.*, **83**, 750 (1961);

(b) D. W. Setser and B. S. Rabinovitch, *Can. J. Chem.*, **40**, 1425 (1962).

(4) H. M. Frey and I. D. R. Stevens, *Proc. Chem. Soc.*, **79** (1962).