ide in 50 ml of 95% ethanol. The thiophenoxide solution was added dropwise to the chloride solution with stirring. After 4 hr, the solution was poured into 400 ml of water. The solution was extracted twice with 150-ml portions of ether. The ether layer was washed twice each with 100 ml of dilute potassium hydroxide solution and 100 ml of water and dried ($MgSO_4$), and the ether was removed in vacuo. The residual oil was dissolved in 100 ml of glacial acetic acid, and the solution was chilled in an ice–water bath. To this solution was added dropwise 20 ml of 30% hydrogen peroxide. After standing overnight at room temperature, the solution was poured into 500 ml of water and extracted twice with 150-ml portions of ether. The ether extracts were combined and washed once with 200 ml of water and twice with 150 ml of saturated sodium bicarbonate solution followed once by 200 ml of water. The ether was dried with anhydrous magnesium sulfate and removed in vacuo. Crystallization from dichloromethane–Skellysolve B gave 8.93 g (45%) of **2b**: mp 112°; ir (KBr) 1700 (C=O), 1310 and 1150 cm^{-1} (SO_2); NMR ($CDCl_3$) 1.42 (t, J = 7 Hz, 3 H), 4.35 (s, 2 H), 4.40 (q, J = 7 Hz, 2 H), and 7.0–8.0 ppm (m, 9 H).

Anal. Calcd for $C_{16}H_{16}O_4S$: C, 63.16; H, 5.26. Found: C, 62.88; H, 5.33.

α-Bromo-*p*-Carbethoxybenzyl Phenyl Sulfone (1b). One gram (3.0 mmol) of **2b** was dissolved in 15 ml of dry DMF in a dry 50-ml three-necked flask under a dry nitrogen atmosphere. To the solution was added 200 mg (4.15 mmol) of 50% sodium hydride in oil dispersion. The solution turned dark yellow in color and was heated to 60° for 10 min. The solution was cooled to room temperature and transferred via syringe into a solution containing 400 mg (3.78 mmol) of cyanogen bromide in 25 ml of dry DMF. A reddish brown color appeared. After 15 min, the solution was poured into 200 ml of water and extracted twice with 50-ml portions of dichloromethane. The dichloromethane solution was washed twice with sodium thiosulfate solution followed by water and dried ($MgSO_4$), and the solvent was removed in vacuo. Crystallization from methylene chloride–Skellysolve B gave 460 mg (37%) of **1b**: mp 112°; ir (KBr) 1710 (C=O), 1325 and 1150 cm^{-1} (SO_2); NMR ($CDCl_3$) 1.42 (t, J = 7 Hz, 3 H), 4.40 (q, J = 7 Hz, 2 H), 5.81 (s, 1 H) and 7.2–8.1 ppm (m, 9 H).

Anal. Calcd for $C_{16}H_{15}BrO_4S$: C, 50.13; H, 3.95. Found: C, 50.25; H, 4.12.

α-Bromo-*p*-carboxylbenzyl Phenyl Sulfone (1a). To a solution of 500 mg (1.49 mmol) of **1b** in 50 ml of 75% ethanol was added 50 ml of 4% potassium hydroxide in 75% ethanol. After 4 hr, hydrochloric acid was added until the solution was acidic. From this solution precipitated 330 mg (100%) of **1a**: mp 252°; ir (KBr) 3200–2400 (OH), 1690 (C=O), 1300 and 1150 cm^{-1} (SO_2); NMR (Me_2SO-d_6) 4.3–5 (1 H), 6.94 (s, 1 H), and 7.4–8 ppm (m, 9 H).

Anal. Calcd for $C_{14}H_{11}BrO_4S$: C, 47.34; H, 3.12. Found: C, 47.22; H, 2.97.

***p*-Methylsulfonylbenzyl Phenyl Sulfone (2c).** In a two-neck 300-ml flask, 3.4 g (0.020 mol) of *p*-methylsulfonyltoluene (Aldrich) was dissolved in 50 ml of dry carbon tetrachloride. The solution was brought to reflux and a bromine solution of 3.5 g (0.022 mol) in 20 ml of carbon tetrachloride was added dropwise (ca. 30 min) while the flask was illuminated with a 275-W sun lamp. After 1 hr, an NMR spectrum showed a mixture of starting material (5%), α-bromo-*p*-methylsulfonyltoluene, (75%) and α,α-dibromo-*p*-methylsulfonyltoluene (20%). The solvent was removed by rotary evaporation and 20 ml of hexane added. The resulting precipitate (2.7 g) was collected and shown by NMR spectroscopy to be a mixture of α-bromo-*p*-methylsulfonyltoluene (60%) ($-CH_2Br$, δ 4.47) and α,α-dibromo-*p*-methylsulfonyltoluene (40%) ($CHBr_2$, δ 6.69). The mother liquor gave 0.9 g of the monobromide, mp 93–94° (lit.[12] 94–96°).

The mixture of 2.7 g of the monobromide and dibromide (vide supra) and 6.0 g of sodium benzenesulfinate in 70 ml of dry dimethyl sulfoxide was heated at 90–100° for 30 min. The progress of the reaction can be followed conveniently by TLC (dichloromethane, silica gel). The mixture was poured into 600 ml of water, and the precipitate was collected and recrystallized from acetonitrile to give 1.9 g (50% based on 2.7 g of the mixture of bromides) of **2c**: mp 261–262°; NMR ($CDCl_3$) 3.04 (s, 3 H), 4.40 (s, 2 H), and 7.1–7.7 ppm (m, 9 H).

Anal. Calcd for $C_{14}H_{14}O_4S_2$: C, 54.17; H, 4.54. Found: C, 54.25; H, 4.50.

α-Bromo-*p*-methylsulfonylbenzyl Phenyl Sulfone (1c). Compound **1c** was prepared from **2c** following the same procedure used to convert **2b** to **1b**. One gram of **2c** gave 0.63 g (50%) of **1c**: mp 178–179° (*acetonitrile*); NMR ($CDCl_3$) 3.04 (s, 3 H), 5.78 (s, 1 H), and 7.2–7.9 ppm (m, 9 H).

Anal. Calcd for $C_{14}H_{13}BrO_4S_2$: C, 43.19; H, 3.37. Found: C, 43.31; H, 3.32.

The syntheses of **3a, 3b, 4a** and **4b** were reported earlier.[2]

Kinetic Procedure. The rates for compounds **1a, 1b, 3a, 3b, 4a,** and **4b** were determined by the conductance method.[2] The rate of reaction of **1c** was determined by the spectrophotometric technique.[2] All runs were made in at least duplicate. The precision in the rate constants reported in Tables I–III is ±5%. The σ^- values reported were determined from log $k_X = \sigma^-$ (5.97) + (−5.970) where X = *p*-COOH, *p*-$COOC_2H_5$, and *p*-CH_3SO_2, k_X are the rate constants at 25° reported in Tables I and II, and −5.970 is log k_H[2] at 25°. The σ^- values reported have a precision of ±0.02 units.

Acknowledgment. Support from the University of Maryland Computer Science Center is gratefully acknowledged.

Registry No.—**1a**, 56571-76-7; **1b**, 56571-77-8; **1c**, 56571-78-9; **2b**, 56571-79-0; **2c**, 56571-80-3; **3a**, 41037-90-5; **3b**, 51229-69-7; **4a**, 41037-91-6; **4b**, 51229-70-0; TPP, 603-35-0; *p*-toluoyl chloride, 874-60-2; sulfuryl chloride, 7791-25-5; thiophenol, 108-98-5; cyanogen bromide, 506-68-3; *p*-methylsulfonyltoluene, 3185-99-7; α-bromo-*p*-methylsulfonyltoluene, 53606-06-7; α,α-dibromo-*p*-methylsulfonyltoluene, 33460-70-7; sodium benzensulfinate, 873-55-2.

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[α,α-$^2H_2$]Dibenzyl Sulfoxide. Synthesis, Reactions, and Chiroptic Properties

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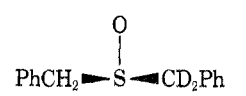
We wish to report on the synthesis, some reactions, and the chiroptic properties of (*R*)- and (*S*)-[α,α-$^2H_2$]dibenzyl sulfoxide (**1**), dissymmetric by substitution of deuterium for hydrogen, two bonds from the asymmetric sulfur atom.



(*R*)-**1**

Optical activity in molecules whose dissymmetry arises from isotopic differences is well known and has been observed in compounds containing the isotope pairs ^1H–^2H, ^{16}O–^{18}O, and ^{12}C–^{13}C. Chiroptic properties of these com-

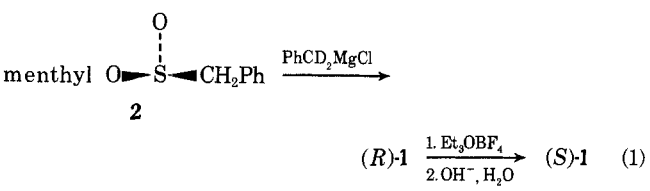
pounds have often been difficult to obtain because of their low rotation, combined, in many cases, with a highly absorbing chromophore such as an aromatic ring. Nevertheless, the first extrema of Cotton effects were observed in the ORD spectra of (*R*)-[1-^{2}H]-1-butyl acetate,[2] (*R*)- and (*S*)-[1-^{2}H]succinic acid,[3] and several imines of the general structure RR′CNCHDR″.[4] Both extrema were observed for (*R*)-[1-^{2}H]-*N*-(isopropylidene)neopentylamine, which unlike the other imines studied, does not have R or R′ equal to phenyl. The CD spectra of (1*R*)-[1-^{2}H]-α-fenchocamphoronequinone[5] and (*S*)-[4-^{2}H][2.2]paracyclophane[6] have recently been reported.

The CD spectrum of (1*R*)-[2-^{18}O]-α-fenchocamphoronequinone has been recorded and is the only example of chiroptical measurements on an ^{16}O–^{18}O dissymmetric molecule.[7] The other optically active ^{16}O–^{18}O compounds, all aryl sulfones,[8] have unfavorable rotation to absorption ratios which precluded CD or ORD measurements of Cotton effects.

Cotton effect measurements on (*R*)- and (*S*)-[α-^{13}C]dibenzyl sulfoxides, the only examples of ^{12}C–^{13}C dissymmetric molecules for which optical activity has been detected, were similarly thwarted.[9]

The ^{1}H–^{2}H compounds cited above, except for the quinone and the paracyclophane, all contain a monodeuterium substituted methylene group as the center of chirality which asymmetrically perturbs a symmetric chromophore, but in sulfoxide **1**, the deuterium atoms are two bonds away from the asymmetric center.

Sulfoxide (*R*)-**1** was synthesized by treating (R_S)-menthyl phenylmethanesulfinate (**2**) with the Grignard reagent prepared from [α,α-^{2}H$_2$]benzyl chloride,[10] and converted to its enantiomer by ethylation followed by alkaline hydrolysis (eq 1).



(1)

The enantiomeric purity of (*R*)-**1** was calculated to be 96% based on the highest rotation reported for **2** and assuming that the transformation of **2** to (*R*)-**1** proceeded with complete inversion. The conversion of (*R*)-**1** to (*S*)-**1** proceeded with 89% inversion based on their rotations at 300 nm.

The ORD and CD spectral data for (*R*)-**1** and the ORD data for (*S*)-**1**, measured from 300 to 250 nm in 95% ethanol and in chloroform, are given in Table I together with uv spectral data obtained on racemic **1**. The chiroptic spectra for **1** are depicted in Figure 1. Since the ORD curve for (*S*)-**1** was simply a mirror image of that for (*R*)-**1**, although diminished in magnitude by about 0.8, it is not shown.

Several small Cotton effects superimposed on a positive background, apparent in both the ORD and CD spectra (EtOH) and shown in Figure 1, occur in the $^1L_b \leftarrow {}^1A$ region of uv absorption.

The shape of the ORD curve of (*R*)-**1** was the same in chloroform as it was in ethanol. Sign changes, ascribed to conformational differences, have been observed for some alkyl benzyl sulfoxides[11] when the solvent was changed from ethanol to chloroform.

Since ^{1}H and ^{2}H have almost the same electronic and steric properties, it is unlikely that the chiroptic behavior of our compound is due to electronic or steric perturbations of the chromophore. It is more likely that $PhCH_2$ vibronic

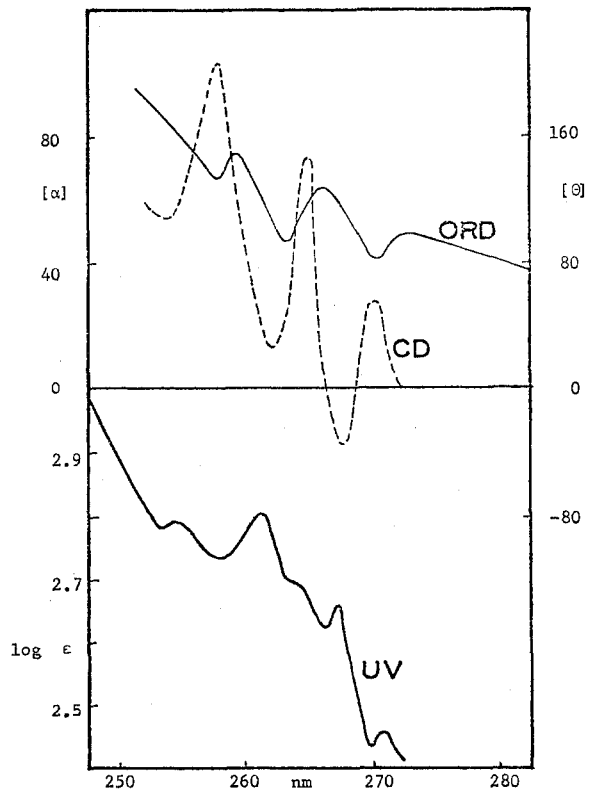


Figure 1. ORD, CD, and uv spectra of **1** in 95% EtOH.

Table I
Optical Rotatory Dispersion, Circular Dichroism, and Ultraviolet Spectra of $PhCH_2SOCD_2Ph$

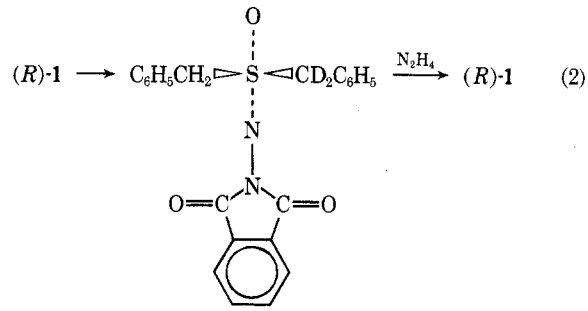
Compd	Spectral values[e]
(*R*)-**1**[a]	23 (300), 30 (290), 40 (280), 47 (275), 49 (272.5 P), 41 (270 T), 65 (266 P), 45 (263 T), 75 (259 P), 66 (258 T), 80 (255), 102 (250)
(*S*)-**1**[a]	−18 (300), −23 (290), −31 (280), −42 (275), −45 (272.5 T), −32 (270 P), −58 (266 T), −37 (263 P), −37 (263 P), −62 (259 T), −59 (258 P), −66 (255), −91 (250)
(*R*)-**1**[b]	0 (272), 56 (270 Mx), −38 (267.5 Mi), 147 (265 Mx), 23 (262 Mi), 205 (258 Mx), 103 (254 Mi), 119 (252)
(*R*)-**1**[c]	0.69 (300), 0.82 (290), 0.99 (280), 1.68 (275), 2.46 (271 Mx), 2.43 (270 Mi), 2.66 (267 Mx), 2.62 (266 Mi), 2.66 (265 If), 2.70 (263 If), 2.81 (261 Mx), 2.77 (2.59 If), 2.73 (257.5 Mi), 2.79 (254 Mx), 2.78 (253 Mi), 2.81 (252), 2.99 (247.5), 3.13 (245), 3.32 (242.5)
(*R*)-**1**[d]	34 (300), 40 (290), 57 (280), 92 (274 P), 70 (271 T), 116 (267 P), 64 (264 T), 123 (261 P), 115 (258 T), 182 (250)

[a] ORD in 95% ethanol, specific rotation (nm), *c* 8.3–0.69 mg/ml. [b] CD in 95% ethanol, molecular ellipticity (nm), *c* 0.83 mg/ml. [c] Uv in 95% ethanol, log ε (nm), 8.3–0.17 mg/ml. [d] ORD in chloroform, specific rotation (nm), 0.73–0.29 mg/ml. [e] P = peak, T = trough; Mx = maximum, Mi = minimum, If = inflection.

interactions differ significantly from $PhCD_2$ vibronic interactions and, consequently, lead to an appreciable rotatory strength. Specifically, it appears as if there is a coupling of aromatic molecular vibrations with electron motions which shows up in an electronic transition of the $^1L_b \leftarrow {}^1A$ type. Recently, other workers have presented theoretical arguments and experimental evidence to account for rotatory

strength in (−)-(*S*)-[4-^{2}H][2.2]paracyclophane via a similar vibronic coupling mechanism.[6,12]

Sulfoxide (*R*)-1 was converted to (*R*)-sulfoximine **3** which, upon hydrazinolysis, gave back partially racemized (*R*)-1 with 75% retention of configuration (eq 2).[13]



(2)

3

While this showed **3** to be nonracemic, **3** was not a detectably optically active compound. It formed strongly absorbing, yellow solutions which precluded chiroptic measurements in the region of interest; in fact, no rotation was observed at any wavelength. The cause for the partial racemization is not known, but 1 was observed to undergo partial racemization in chloroform solution. Thus, the process depicted in eq 2 may be completely stereospecific with the loss of optical activity resulting from the racemization of 1 in processes not involving the formation or hydrazinolysis of **3**.

Experimental Section

The ORD–CD spectra were recorded using a Cary 60 spectropolarimeter, the uv spectra using a Cary 14 spectrophotometer, the NMR using a Varian XL-100 spectrometer, and the mass spectra using an RMU Hitachi 6D spectrometer.

(*R*)-[α,α-^{2}H$_2$]Dibenzyl Sulfoxide (1). (R_S)-Menthyl phenylmethanesulfinate (**2**, 3.09 g, 10.5 mmol), [α]D +105° ($CHCl_3$), in ether (15 ml) was added at −40° to a solution of the Grignard reagent prepared from [α,α-^{2}H$_2$]benzyl chloride (1.6 g, 12.4 mmol) and magnesium (0.26 g, 0.011 g-atom) in ether (50 ml). The mixture was stirred at −40° for 2 hr, kept at room temperature overnight, and then heated at reflux for 1 hr. The usual work-up afforded, after column chromatography (silica, ethyl ether) (*R*)-1 (1.59 g, 6.82 mmol) in 65% yield: mp 127–128° (lit. mp 131–134°); mass spectrum *m/e* (rel intensity) 230 (3), 231 (2), 232 (93), 234 (2); NMR ($CDCl_3$) δ 3.86 (q, 2.06, J = 12.5 Hz, CH_2), 7.33 (m, 10.0, C_6H_5).

(*S*)-[α,α-^{2}H$_2$]Dibenzyl sulfoxide (1) was synthesized from (*R*)-1, $[\alpha]_{300}$ +23° (EtOH) (41 mg, 0.18 mmol), by ethylation with triethyloxonium tetrafluoroborate (53 mg, 0.28 mmol) in methylene chloride (6 ml) followed by hydrolysis in rapidly stirred 1% sodium hydroxide solution; 98% yield, 40.2 mg, $[\alpha]_{300}$ −18° (EtOH).[14]

(*R*)-*N*-Phthalimido[α,α-^{2}H$_2$]-*S*,*S*-dibenzyl sulfoximide (3) was synthesized from (*R*)-1 with a reaction time of 2 hr in 65% yield (ethanol), mp 150° dec.[13] Isotopically normal sulfoximide **3** was similarly obtained in 74% yield, mp 152° dec.

Anal. Calcd for $C_{22}H_{18}N_2O_3S$: C, 67.67; H, 4.64; N, 7.17. Found: C, 67.50; H, 4.56; N, 7.16.

Hydrazinolysis of Sulfoximide 3.[13] Hydrazine hydrate (98%, 1.5 ml) was added to a stirred suspension of sulfoximide **3** (0.13 g) in ethanol (5 ml) at room temperature. After 30 min, ether (100 ml) was added. The organic layer was dried over sodium sulfate and concentrated, and the residue was chromatographed (silica, ether) to give (*R*)-1 (75 mg, 0.32 mmol) in 97% yield, mp 128°.

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Registry No.—(*R*)-1, 54976-21-5; (*S*)-1, 56804-68-3; **2**, 21204-21-7; **3** isomer A, 56804-69-4; **3** isomer B, 33296-98-9; [α,α-^{2}H$_2$]benzyl chloride, 33712-34-4, hydrazine, 302-01-2.

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Reactions of Undecyl Radicals with Substituted Toluenes

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Since we underscored the importance of establishing the slopes of Hammett correlations in hydrogen abstractions from substituted toluenes by alkyl radicals,[2] several reports have appeared which indicate that ρ is positive for benzyl hydrogen abstractions by *tert*-butyl,[3] undecyl,[4,5] and 3-heptyl[6] radicals. All of these determinations but one[5] were based on measurements of the amount of alkane produced; it was concluded that formation of alkane occurs only by abstraction of benzylic hydrogens and not also by addition to the aromatic nucleus and subsequent reactions of the alkyl radicals with products derived thereby,[7] or by disproportionation of the alkyl radicals themselves. The one determination based on measurements of reactant disappearance (NMR of methyls of the toluenes) was also the only one to include *p*-methoxytoluene among the substrates.[5]

We wish to make available some of our measurements that are relevant to this topic. We have determined the relative reactivities of substituted toluenes toward undecyl radicals in benzene solvent by measuring the disappearance of the aromatics by gas–liquid chromatography in the usual way.[2] We have measured also the reactivities of some substituted benzenes, by the same procedure. The results are given in Table I. The "total" reactivity values for the toluenes cannot be apportioned quantitatively between addition to the ring and abstraction from the side chain by comparison with the similarly substituted benzenes, because the effect of the methyl on ring addition cannot be taken into account quantitatively on the basis of existing knowledge. However, qualitative comparisons can be made; e.g., in comparing the methoxytoluenes to anisole, clearly the reactivity of anisole includes ring addition and hydrogen abstraction from the methoxy group, if any.

Our results show that the reactivity of *p*-cyanotoluene is