Enantiomerically Pure (*R*)-(+)-2-Phenylethanol-2-*d* and -*1,1,2*-d_3, and (*S*)-(+)-1-Phenylethane-*1*-*d*, -*1,2*,-d_2, -*1,2,2*-d_3, and -*1,2,2,2*-d_4

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(*R*)-(−)-Mandelic acid has been converted by stereospecific reactions into enantiomerically pure (*R*)-(+)-2-phenylethanol-2-*d* ($PhCHDCH_2OH$, $[\alpha]^{20}_D$ +1.52 ± 0.02°, neat), (*R*)-(+)-2-phenylethanol-*1,1,2*-d_3 ($PhCHDCD_2OH$, $[\alpha]^{20}_D$ +1.44 ± 0.02°, neat), and the four (*S*)-(+)-deuteriophenylethanes prepared by replacing the hydroxyl groups of these 1-phenylethanols by hydrogen or deuterium. The optical rotation of (*S*)-(+)-1-phenylethane-*1*-*d* ($PhCHDCH_3$, $[\alpha]^{20}_D$ +0.81 ± 0.01°, neat) was only slightly different than that of (*S*)-(+)-1-phenylethane-*1,2,2,2*-d_4 ($PhCHDCD_3$, $[\alpha]^{20}_D$ +0.79 ± 0.01°, neat), while the corresponding di- and trideuterated analogues had the same rotation within experimental limits ($[\alpha]^{20}_D$ +0.80 ± 0.01°, neat).

Our studies on hydrogen vs. deuterium transfer in asymmetric reductions[2] required enantiomerically pure 2-phenylethanol-2-*d* ($PhCHDCH_2OH$, **1a**) and 2-phenylethanol-*1,1,2*-d_3 ($PhCHDCD_2OH$, **1b**) as intermediates for preparation of optically active reducing agents which were chiral by virtue of deuterium substitution. Our initial synthesis of the latter gave a product which was only 74% enantiomerically pure,[2] and we have been unsuccessful with the published[3] synthesis of the former. During these studies, we became aware of certain inconsistencies in the literature concerning both the sign and magnitude of rotation of **1a** and **1b** which required clarification.

The pertinent data from the literature reports[2-5,7] concerning these compounds are summarized in Table I. Entry 1 reports the configuration of **1a** as *R*-(+) and entries 5 and 6 report the configuration of **1b** as *R*-(+) [or the equivalent *S*-(−)], while entries 2 and 3 report the configuration of **1a** as *R*-(−) and entry 4 reports the configuration of **1b** as *R*-(−).[6] Furthermore, the reported magnitudes of the calculated maximum specific rotations, regardless of sign, vary from $[\alpha]^{20-28}_D$ 1.41 to 1.98° (neat). Although it seemed extremely unlikely, it was conceivable that there was a substantial difference in optical rotation of **1a** and **1b**. Clearly, these reports need to be reconciled or corrected.

In these studies we planned to check the absolute configuration and enantiomeric purity of the carbinols **1a** and **1b** by conversion into the corresponding (1-deuterioethyl)benzenes **2a–d** (eq 1 and 2), for which there was ample data.[8-12] It

$$\underset{\textbf{1a}}{PhC^*HDCH_2OH} \xrightarrow[\text{(2) } LiAlH_4 \text{ (or } LiAlD_4)]{\text{(1) tosyl Cl}} \underset{\textbf{2a}}{PhC^*HDCH_3} \quad (\text{or } PhC^*HDCH_2D,\ \textbf{2b}) \qquad (1)$$

$$\underset{\textbf{1b}}{PhC^*HDCD_2OH} \xrightarrow{\text{as above}} \underset{\textbf{2c}}{PhC^*HDCD_2H} \quad (\text{or } PhC^*HDCD_3,\ \textbf{2d}) \qquad (2)$$

seemed likely that the optical rotations for 1-phenylethane-*1*-*d* (**2a**), -*1,2*-d_2 (**2b**), -*1,2,2*-d_3 (**2c**), and -*1,2,2,2*-d_4 (**2d**) would be very nearly the same. However, our original results, using the method of Tomaszewski,[12] gave a product **2c** (entry 6, Table II) whose rotation was substantially greater than the literature values for **2a**. This was not too surprising because of the inherent difficulties in determining the enantiomeric purity of hydrocarbons and in view of the inference by Eliel and Arigoni[13] that the maximum rotation reported for **2a**, $[\alpha]^{20}_D$ 0.80° (neat), "might be substantially too low." A further discrepancy in the literature is revealed by the data for **2a** shown in Table II. The first four entries give the configuration of **2a** as *R*-(−) or the equivalent *S*-(+), but the fifth entry gives the rotation of **2a** as *S*-(−). Again it is required that these incongruities be reconciled or corrected. Accordingly, we undertook a critical study of the synthesis and optical rotation of **1a** and **1b** as well as the (1-deuterioethyl)benzenes **2a–d**.

Results and Discussion

In order to eliminate differences between the compounds which might arise as artifacts from the method of synthesis, we chose to derive all compounds from the same batch of starting material, utilizing the same reaction sequences and the same source of deuterium. The approach is outlined in Scheme I.

Scheme I

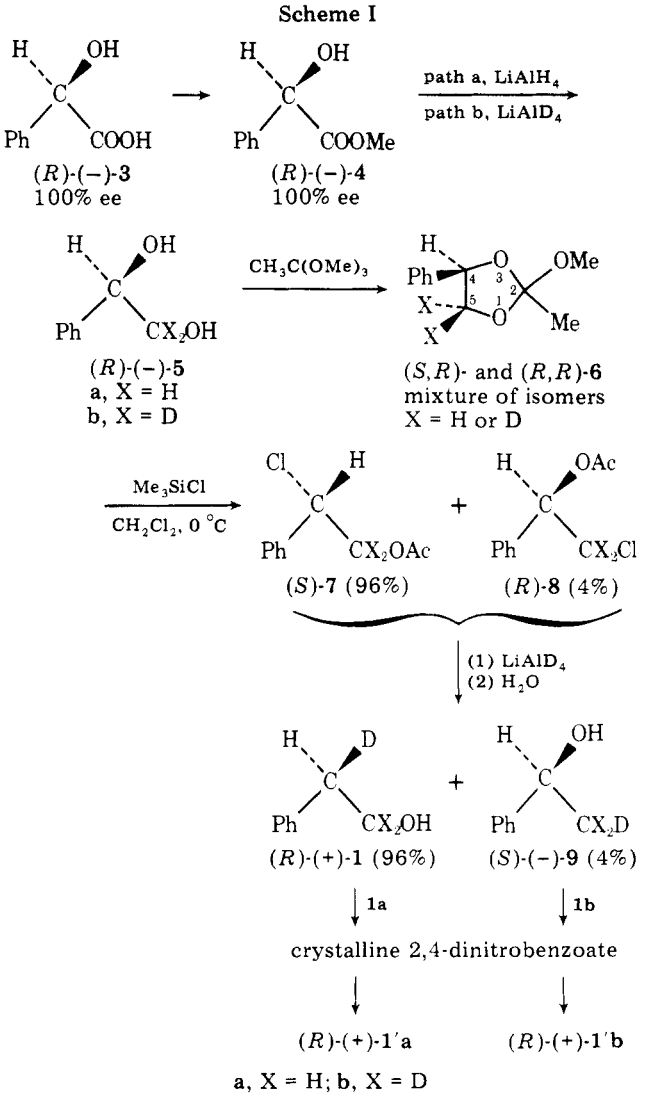

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Table I. Reported Rotations of 2-Phenylethanol-*2-d* (1a) and 2-Phenylethanol-*1,2,2-d*$_3$ (1b)

entry	starting material configuration and enantiomeric purity (% ee)	deuterium source at chiral center	product[a] **1a** or **1b** configuration	specific rotation (calcd as per notes $[\alpha]_{max}$ (neat, °C), deg	ref
1	(*R*)-mandelic acid (97)	$LiAlD_4$	(*R*)-(+)-PhCHDCH$_2$OH	+1.738 (27)[b]	3
2	(*S*)-mandelic acid (99)	$LiEt_3BD$	(*R*)-(−)-PhCHDCH$_2$OH	−1.98 (20)[c,d]	4
3	(*S*)-benzyl-1-*d* alcohol (81)	D_2O	(*R*)-(−)-PhCHDCH$_2$OH	−1.51 (28)[e]	5, 6
4	(*S*)-benzyl-*1*-*d* alcohol (73)	D_2O	(*R*)-(−)-PhCHDCD$_2$OH	−1.41 (25)[f]	6
5	(*S*)-mandelic acid (90)	$NaBD_3CN$	(*R*)-(+)-PhCHDCD$_2$OH	+1.46 (25)[g]	7
6	(*R*)-mandelic acid (99)	$LiAlD_4$	(*S*)-(−)-PhCHDCD$_2$OH	−1.46 ± 0.03 (20)[h]	2

[a] Percent deuteration at chiral benzylic position in each case was reported to be better than 98%; the configuration is assumed based on the method of synthesis. [b] Corrected for 97% ee (enantiomeric excess) based on the purity of starting material. [c] Calculated for product which was 94% chemically pure. [d] Enantiomeric purity was determined by us on a sample supplied by authors[4] using chiral shift reagent Eu(dcm)$_3$,[2,14] but amount was not sufficient to confirm rotation. [e] Calculated from results of entry 4. [f] Based on sample reported to be 75% enantiomerically pure.[5] [g] Based on our maximum value[2] reported in entry 6. [h] Based on chiral shift reagent studies.[2]

Table II. Reported Rotations for 1-Phenylethane-*1-d* (2a)

entry	starting material configuration (% ee)	deuterium source	product **2a** configuration[a] (% ee)	specific rotation (calcd as per notes) $[\alpha]_{max}$ (neat, °C),[b] deg	ref
1	(*S*)-(−)-PhCHClCH$_3$ (42)[c]	$LiAlD_4$/LiD	(*R*)-(−)-PhCHDCH$_3$ (42)	−0.70 ± 0.05 (25)	8
2	Kirkwood's theory		(*S*)-(+)-PhCHDCH$_3$ (100)	+0.41	9
3	(*S*)-(−)-PhCHClCH$_3$ (37)[c]	$LiAlD_4$/LiD	(*R*)-(−)-PhCHDCH$_3$ (37)	−0.78 ± 0.03 (23)	10
4	(*R*)-(+)-PhCHClCH$_3$ (51)[c]	$LiAlD_4$/LiD	(*S*)-(+)-PhCHDCH$_3$ (51)	+0.76 ± 0.05 (26)	11
5	(*R*)-(+)-PhCHDCH$_2$OH (97)[d]	$LiAlD_4$	(*S*)-(−)-PhCHDCH$_3$ (97)	−0.243 (24)	3
6	(*S*)-(−)-PhCHDCD$_2$OH (75)[e]	$LiAlD_4$	(*S*)-(+)-PhCHDCD$_2$H (75)	+2.10 (22)	12

[a] Configuration was based on method of synthesis. [b] Based on enantiomeric purity (% ee) of starting material, neat liquid, d^{20}_4 0.8712. [c] Based on reported $[\alpha]_D$ max 117 ± 7° for starting material.[11,23] [d] Cf. Table I, entry 1. [e] Cf. Table I, entry 6.

Enantiomerically pure (*R*)-(−)-methyl mandelate (**4**) was divided into two portions; one portion was reduced with lithium aluminum hydride ($LiAlH_4$) to (*R*)-(−)-phenylethylene glycol (**5a**) and the other with lithium aluminum deuteride ($LiAlD_4$) to (*R*)-(−)-phenylethylene-*2,2-d*$_2$ glycol (**5b**). Reaction of **5a** and **5b** with trimethyl orthoacetate by the method of Newman[14,15] afforded a nearly equal mixture of (2*R*,4*R*)- and (2*S*,4*R*)-2-methoxy-2-methyl-4-phenyl-1,3-dioxolane (**6**). Subsequent treatment with trimethylsilyl chloride[15] in methylene chloride at 0 °C afforded a mixture of (*S*)-2-chloro-2-phenylethyl acetate (**7**) and (*R*)-2-chloro-1-phenethyl acetate (**8**) in a 96:4 ratio. Newman[14] has shown that this reaction proceeds by a stereospecific S_N2 process by conversion of the mixture of **7** and **8** into enantiomerically pure (*R*)-(+)-styrene oxide.

Direct reduction of the 96:4 mixture of **7** and **8** with $LiAlD_4$ in 1,2-dimethoxyethane (DME) afforded a mixture of 2-phenylethanol (**1**) and 1-phenylethanol (**9**) in a 96:4 ratio. Attainment of the same ratio of **1**/**9** from that of **7**/**8** in this reaction implies that styrene oxide was not an intermediate in this reduction, corroborating the results of Eliel.[16] Low-pressure liquid chromatographic purification of this mixture on silica gel afforded **1** of greater than 99% chemical purity by gas chromatography. Compound **1** was further purified by recrystallization of its 2,4-dinitrobenzoate derivative followed by regeneration of **1** (labeled **1'a** or **1'b**). In several cases this purification resulted in a substantial change in the observed rotations for **1a** and **1b**, which had been shown to be greater than 99% chemically pure by gas chromatography. It is conceivable that the material obtained by others (entries 1 and 2 of Table I) was also contaminated by small amounts of strongly rotating impurities.

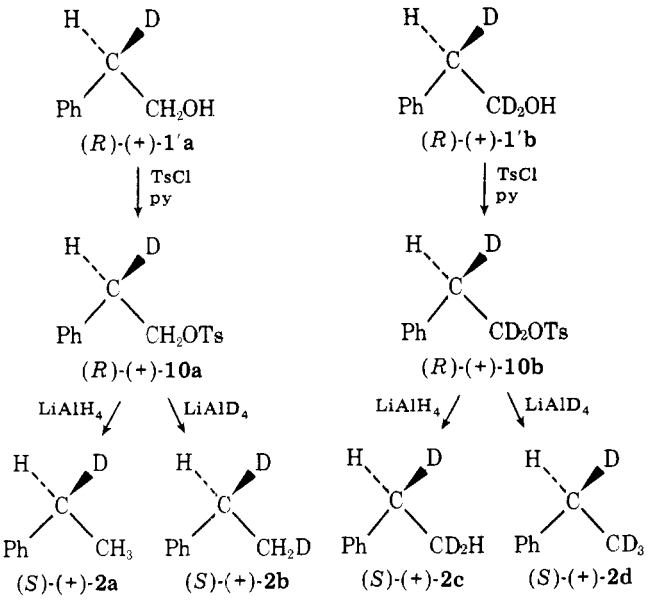
The enantiomeric purities of **1'a** and **1'b** were determined by NMR spectroscopy using Whitesides' chiral shift reagent, Eu(dcm)$_3$.[2,17] The lanthanide-induced shifted spectra of both **1'a** and **1'b** showed that both compounds were enantiomerically pure. Hence, the conversion of mandelic acid, (*R*)-(−)-**3**, to (*R*)-(+)-2-phenylethanol-*2-d* by the method shown in Scheme I proceeded stereospecifically with overall retention (via double inversion) at the asymmetric center.

Assignment of the absolute *R* configuration to (+)-**1a** and (+)-**1b** follows from the well-known mechanistic course of the reactions employed. Therefore, the experimental signs for rotations of **1a** reported by Stephenson and Mattern[4] and of **1a** and **1b** reported by Stille and co-workers[5,6] (entries 2, 3, and 4 of Table I) are in error; however, inspite of the incorrect sign of rotations, the reported configurations must be correct as given in these papers[4,6] and the mechanistic conclusions valid.

Conversion of enantiomerically pure **1'a** and **1'b** into the various deuterated chiral ethylbenzenes **2a–d** was accomplished as outlined in Scheme II. Treatment of **1'a** or **1'b** with *p*-toluenesulfonyl chloride in pyridine afforded the crystalline tosylates. Recrystallization of these constituted further purification. Treatment of both tosylate derivatives with both $LiAlH_4$ and $LiAlD_4$ in dimethoxytetraethylene glycol (tetraglyme) afforded the chiral ethylbenzenes (*S*)-(+)-**2a–d**. Since this conversion does not involve the chiral center, **2a,b** and **2c,d** should possess the same enantiomeric purity as **1a** and **1b**, respectively. VPC analysis of the products showed them to be better than 99% chemically pure; they contained no styrene. Further, ^{13}C NMR of the products established that each deuterated compound contained the designated number of deuterium atoms at the positions shown, each greater than 98 atom % deuterated.[19,20]

The observed rotations for (*S*)-(+)-**2a** and **-2d** were barely different, while those for **2b** and **2c** were the same; our observed rotations for **2a–d** and **1a,b** are shown in Table III along with calculated maximum specific rotations for these deuterated substances. It appears from the values reported in Table III that substitution of deuterium for hydrogen at nonasymmetric centers in the ethylbenzene molecule exerts

Scheme II



only a very slight perturbation upon the observed rotation. In the case of 2-phenylethanol-*2-d* and the *-1,1-d*$_2$ analogue, a significant but small difference was observed.

A comparison of the optical rotation values for the (1-deuterioethyl)benzenes in Tables II and III shows that the original value reported for (*S*)-(−)-PhCHDCH$_3$ by Eliel in 1949 (Table II, entry 1) agrees well with ours both in sign and magnitude. Two of the subsequent values reported (Table II, entries 3 and 4) are identical within experimental error. However, the *S*-(−) value of entry 5 is in error both with respect to sign and magnitude, while that for entry 6 has the correct sign but the magnitude is too high. We conclude that one must use extraordinary care with purity when using optical rotation for determining enantiomeric purity for compounds such as these. It is essential wherever possible that enantiomeric purity be determined by an absolute method[21] such as that using a chiral shift reagent[4,17] or a diastereomeric derivative.[2,22]

Experimental Section

Capillary melting points (Melt-Temp aluminum block) and boiling points are uncorrected. Nuclear magnetic resonance (NMR) spectra, ^{1}H and ^{13}C, and chiral shift reagent studies were carried out on a Varian Associates XL-100 spectrometer;[20] data are reported in parts per million (δ) downfield from tetramethylsilane (Me_4Si) as an internal standard. Signals are designated as s = singlet, d = doublet, t = triplet, q = quartet, b = broad, and m = multiplet. Rotations were recorded as neat liquids or as solutions using a 20.0 °C thermostated 1-dm, 0.8-mL, cell with fixed end plates on a Perkin-Elmer Model 241 electronic polarimeter. 1,2-Dimethoxyethane (DME) was distilled from $LiAlH_4$ under N_2 just prior to use. Tetraglyme was distilled from sodium benzophenone ketyl under N_2 and stored over 4 Å molecular sieves before use. All of the $LiAlD_4$ used in this study was obtained from Ventron, lot no. 081176. All deuterated substrates were found to be better than 98 atom % D by ^{13}C NMR spectroscopy.[19] Vapor phase chromatographic (VPC) analyses were performed on a Hewlett-Packard gas chromatograph, Model 5750, with flame ionization detection using either condition A (8% Carbowax 20M on Chrom G, 80–100 mesh, 6 ft × 2 mm glass column, 60 mL/min He, 185 °C, injector 200 °C, detector 250 °C) or B (10% OV-17 on Chrom G, 80–100 mesh, 6 ft × 2 mm glass column, 60 mL/min He, injector 200 °C, at 8 °C/min). The chiral shift reagent (*d,d*-dicampholylmethanato)-europium(III), Eu(dcm)$_3$, used in this study was prepared according to the method of Whitesides.[17]

(*R*)-(−)-Methyl Mandelate (4). (*R*)-(−)-Mandelic acid (100 g, 0.66 mol; $[\alpha]^{20}_D$ −155.4° (*c* 2.913, 95% EtOH); 100% ee),[23] methanol (42 g, 1.31 mmol), 2,2-dimethoxypropane[24] (68.9 g, 0.65 mmol), and 3 mL of concentrated sulfuric acid were refluxed (4 h), the mixture was concentrated under reduced pressure, and the resulting oil was recrystallized (4 L of petroleum ether, 30–60 °C) to give (*R*)-(−)-methyl mandelate (92 g, 84%): mp 55–56 °C; $[\alpha]^{20}_D$ −176.7° (*c* 4.027, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 3.33 (s, 1 H), 3.73 (s, 3 H), 5.16 (s, 1 H), 7.36 (s, 5 H).

(*R*)-(−)-Phenylethylene Glycol[25] (5a). A solution of 20 g (0.12 mol) of (*R*)-(−)-methyl mandelate in 25 mL of dry DME was added slowly with stirring at 20 °C under nitrogen to 5.0 g (0.132 mol) of $LiAlH_4$ in 300 mL of DME. After stirring for 12 h at 20 °C, the mixture was hydrolyzed (10 mL of saturated NH_4Cl followed by 10 mL of 3 N HCl) and the product was isolated by concentrating the DME layer and ether washings of the salts (first as solids and then in dilute HCl solution) to give a crude yield of 17.5 g, which was recrystallized from 75 mL of benzene–petroleum ether (75:25) to give 12.0 g (73% yield) of **5a**: mp 59–63 °C; $[\alpha]^{20}_D$ −41.2° (*c* 8.54, 95% EtOH) [lit.[23] mp 63–65 °C, $[\alpha]^{20}_D$ −39.7° (*c* 4.33, 95% EtOH)]; ^{1}H NMR ($CDCl_3$) δ 3.18 (broad s, 2 H), 3.64 (d, 1 H, *J* = 7 Hz), 3.67 (d, 1 H, *J* = 5 Hz), 4.77 (dd, 1 H, J_1 = 5 Hz, J_2 = 7 Hz), 7.27 (s, 5 H).

(*R*)-(−)-Phenylethylene-*2,2-d*$_2$ Glycol (5b). The above preparation using $LiAlD_4$ instead of $LiAlH_4$ gave **5b**: mp 67.5–68 °C; $[\alpha]^{20}_D$ −40.6° (*c* 4.88, 95% EtOH); ^{1}H NMR ($CDCl_3$) δ 3.20 (broad s, 2 H), 4.77 (broad s, 1 H), 7.27 (s, 5 H).

(2*RS*,4*R*)-2-Methoxy-2-methyl-4-phenyl-1,3-dioxolane[14,15] (6a). A mixture of 15 g of **5a**, 36 mL of trimethyl orthoacetate, and 0.2 mL of H_2SO_4 was stirred (20 °C, 10 min) followed by heating (50 °C) under reduced pressure. The residual red oil was distilled (bp 87 °C, 0.02 mmHg) to give 19.6 g (93% yield) of **6a**, α^{28}_D −55.5° (neat, *l* = 1) [lit.[14] α^{19}_D −51.8° (neat, *l* = 1)]. NMR showed this to be a mixture of diastereomers: ^{1}H NMR ($CDCl_3$) δ 1.63 (s, 1.32 H), 1.72 (s, 1.68 H), 3.38 (s, 1.68 H), 3.41 (s, 1.32 H), 3.81 (m, 1 H), 4.36 (m, 1 H), 5.11 (dd, 0.44 H), 5.25 (dd, 0.56 H), 7.35 (s, 5 H).

(2*RS*,4*R*)-2-Methoxy-2-methyl-4-phenyl-1,3-dioxolane-*5,5-d*$_2$ (6b). The above procedure using **5b** instead of **5a** gave a 90% yield of **6b**, $\alpha^{26.3}_D$ −54.90° (neat, *l* = 1). The NMR spectrum of **6b** showed no signals at δ 3.81 and 4.36, and those at δ 5.11 and 5.25 were singlets. Otherwise the spectrum was identical with that of **6a**.

(*S*)-(−)-2-Chloro-2-phenethyl Acetate[14,15] (7a). To a solution of 50 mL of CH_2Cl_2 and 19 g (97.9 mmol) of **6a** at 0 °C was added 36 mL of chlorotrimethylsilane. After 2 h at 0 °C the mixture was concentrated under reduced pressure and the residual oil was distilled (0.07 mmHg): yield 18.7 g (96%); bp 72–74 °C; $\alpha^{28.5}_D$ −68.75° (neat,

Table III. Rotation of 2-Phenylethanol-*2-d* (1'a), 2-Phenylethanol-*1,1,2-d*$_3$ (1'b), and 1-Phenylethane-1-*d*, *-1,2-d*$_2$, *-1,2,2-d*$_3$, and *-1,2,2,2-d*$_4$ (2a–d)

entry	compd[a]	observed rotation α^{20}_D (neat, *l* = 1), deg	max specific rotation $[\alpha]^{20}_D$ (neat), deg
1	(*R*)-(+)-PhCHDCH$_2$OH (**1'a**)	+1.564	+1.52 ± 0.02[b]
2	(*R*)-(+)-PhCHDCD$_2$OH (**1'b**)	+1.503	+1.44 ± 0.02[c]
3	(*S*)-(+)-PhCHDCH$_3$ (**2'a**)	+0.710	+0.81 ± 0.01[d]
4	(*S*)-(+)-PhCHDCH$_2$D (**2'b**)	+0.706	+0.80 ± 0.01[e]
5	(*S*)-(+)-PhCHDCD$_2$H (**2'c**)	+0.714	+0.80 ± 0.01[f]
6	(*S*)-(+)-PhCHDCD$_3$ (**2'd**)	+0.713	+0.79 ± 0.01[g]

[a] All compounds were better than 98% deuterated at the indicated positions. VPC analysis failed to detect chemical impurities in these six samples. We were unable to detect the presence of the enantiomer in **1'a** or **1'b** by methods available,[2,4,17] which should have readily detected 1% of the isomer. The method of conversion of **1'a** into **2a** and **2b** and conversion of **1'b** into **2c** and **2d** should give products of the same enantiomeric and isotopic purity as the starting materials. [b–f] Based on densities, d^{20}_4, estimated by the method of McLean and Adams:[18] [b] 1.020; [c] 1.0454; [d] 0.8752; [e] 0.8834; [f] 0.8916; [g] 0.8998.

l = 1) [lit.[15] α^{19}_D −67.95° (neat, l = 1), $[\alpha]^{21}_D$ +88.54° (c 0.0324, $CHCl_3$)]. The NMR spectrum in the acetate region showed that the product was a mixture of **7** and **8** in a 96:4 ratio: ^1H NMR of **7a**, ($CDCl_3$) δ 2.0 (s, 3 H), 4.42 (d, 2 H, J = 7 Hz), 5.05 (t, 1 H), 7.30 (s, 5 H).

(*S*)-(−)-1-Chloro-2-phenethyl-*1,1-d*$_2$ Acetate (8b). The above procedure using **6b** in place of **6a** gave a 96:4 mixture of **7b** and **8b**: $[\alpha]^{20.0}_D$ +93.7° (c 4.03, $CHCl_3$); ^1H NMR ($CDCl_3$) of **7b**, δ 2.03 (s, 3 H), 5.08 (broad s, 1 H), 7.38 (s, 5 H).

(*R*)-(+)-2-Phenylethanol-*2-d*$_1$ (1a). A suspension of 4.76 g (0.113 mol) of $LiAlD_4$ in 200 mL of dry DME was stirred at 20 °C for 0.5 h, after which was added a solution of 18 g (0.907 mol) of the 96:4 mixture of chloroacetates **7a** and **8a** in 75 mL of dry DME. After stirring (7 h, 20 °C), the mixture was hydrolyzed (10 mL of saturated NH_4Cl followed by 23 mL of 3 N HCl) and the organic layer and ether extracts of the salts were combined. For complete recovery it is necessary to dissolve the salts in dilute HCl and extract further with ether. The combined extracts were dried ($MgSO_4$) and concentrated to give 11.2 g of a crude yellow residue which was distilled: 9.3 g (83% yield); 89–90 °C (2.8 mm). VPC analysis (condition A) showed 96% **1a** and 4% **9a**, α^{20}_D +2.386° (neat, l = 1). Low-pressure preparative chromatography (Woelm silica gel, 0.032–0.063 mm; 2.5 cm × 1.5 m column; ethyl acetate–cyclohexane, 20:80; flow rate 3 mL/min) of 4.0 g of this oil gave 125 mg of **9a** (in the fraction from 1260 to 1360 mL) and 3.47 g of better than 99% pure **1a** (in fractions from 1540 to 2300 mL). Bulb-to-bulb distillation of this latter fraction gave 3.23 g of (*R*)-(+)-**1a**, which was better than 99% pure by VPC: α^{20}_D +1.583°, α^{20}_{546} +1.919°, α^{20}_{436} +3.605°, α^{20}_{365} +6.437° (neat, l = 1); ^1H NMR ($CDCl_3$) δ 2.71 (tt, 1 H, J_{HH} = 7 Hz, J_{HD} = 2 Hz), 3.05 (s, 1 H), 3.69 (d, 2 H, J = 7 Hz), 7.17 (s, 5 H); the ^{13}C proton-decoupled NMR spectrum was consistent with this structure and confirmed the better than 99% deuteration at the benzylic position.

(*R*)-(+)-2-Phenylethanol-*1,1,2-d*$_3$ (1b). Repetition of the above procedure starting with the dideuterio **7b** gave chromatographically purified product **1b** with the expected ^1H and ^{13}C NMR spectra and VPC analysis indicating better than 99% chemical purity and deuterium substitution at the benzylic position: α^{20}_D +1.451°, α^{20}_{578} +1.523°, α^{20}_{546} +1.765°, α^{20}_{436} +3.336° (neat, l = 1).

Purification of 1a and 1b via Their 2,4-Dinitrobenzoate Esters. In separation experiments, the above 2-phenylethanols **1a** and **1b** were converted with purified 2,4-dinitrobenzoyl chloride and pyridine into the 2,4-dinitrobenzoates in theoretical yield. These were purified by recrystallization from about 15 times their amount of 80:20 95% EtOH–EtOAc to give a 73% purified yield. **1b**: mp 110–110.3 °C (lit. mp 108 °C); $[\alpha]^{20}_D$ −0.495 ± 0.02° (c 5.86, EtOAc).

The 2,4-dinitrobenzoates were hydrolyzed (five volumes of 2 N KOH in CH_3OH, 20 °C, 4 h) and processed (CH_2Cl_2 extraction) to give a distilled product (bulb-to-bulb, 85% recovery) which was better than 99.9% pure by VPC. **1'a**: α^{20}_D +1.564°, α^{20}_{578} +1.637°, α^{20}_{546} +1.898°, α^{20}_{436} +3.568°, α^{20}_{365} +6.370° (neat, l = 1). **1'b**: α^{20}_D +1.503°, α^{20}_{579} +1.574°, α^{20}_{546} +1.825°, α^{20}_{436} +3.441°, α^{20}_{365} +6.170° (neat, l = 1). These results are compared with previous literature values in Table I.

Alcohols **1'a** and **1'b** (7 mg in 0.2 mL of $CDCl_3$) in the presence of Eu(dcm)$_3$[17] (75 mg) gave single benzylic proton signals at 1520 Hz (**1'a** was ^1H decoupled at 3000 Hz) with no observable signal for the *S* enantiomer[2] at 1470 Hz. Control experiments showed that the method was capable of detecting 1% of the enantiomer. Therefore, **1'a** and **1'b** are enantiomerically pure within the sensitivity of this method.

(*R*)-(+)-2-Phenylethyl-*2-d* Tosylate[3] (10a). Alcohol **1'a** [4.12 g, α^{20}_D +1.564° (neat, l = 1] was converted to the tosylate[3] (8.9 g crude yield) which was recrystallized from ether–pentane to give 7.34 g (79% yield): mp 37.5–38.5 °C; $[\alpha]^{20}_D$ +0.46 ± 0.01° (c 11.3, ether). Note that this product has the opposite sign and twice the magnitude of the literature value:[3] mp 38.5–39.0 °C; $[\alpha]^{26}_D$ −0.221° (c 10, ether). Compound **10b** was similarly prepared in 91% recrystallized yield: mp 37.8–38.5 °C; $[\alpha]^{20}_D$ +0.46° (c 10.8, ether).

(*S*)-(+)-1-Phenylethane-*1-d* (2a). A 50-mL flask containing $LiAlH_4$ (0.75 g, 19.7 mmol) in 25 mL of tetraglyme was evacuated with stirring (20 °C, 0.05 mmHg, Teflon stirring bar) to remove any volatile impurities. To this was added tosylate **10a** (3.5 g, 12.6 mmol). The flask was carefully reevacuated (0.05 mmHg), and the mixture was heated (20 min at 20 °C, 15 min at 60 °C) to give 1.30 g, 96% yield, of **2a** in a cold trap (−78 °C): 99% chemically pure by VPC condition B; retention time 4.75 min (styrene, retention time 6.7 min, could not be detected). This material was dried (4 Å molecular sieves) and distilled (bulb-to-bulb). The optical rotation and ^1H and ^{13}C NMR properties are tabulated in Table IV and below.

(*S*)-(+)-1-Phenylethane-*1,2-d*$_2$ (2b), (*S*)-(+)-Phenylethane-*1,2,2-d*$_3$ (2c), and (*S*)-(+)-1-Phenylethane-*1,2,2,2-d*$_4$ (2d). The procedure described above for **2a** was repeated using $LiAlD_4$ instead of $LiAlH_4$ starting with **1'a** and using **1'b** with both $LiAlH_4$ and $LiAlD_4$ to give **2c** and **2d**. The optical rotations, $\alpha^{20}_{wavelength}$ (neat, l = 1), were all positive and are tabulated in Table IV.

Table IV[a]

	α^{20}_D	α^{20}_{578}	α^{20}_{546}	α^{20}_{436}	α^{20}_{365}
2a	0.710	0.743	0.861	1.604	2.843
2b	0.708	0.740	0.857	1.600	2.835
2c	0.714	0.748	0.866	1.615	2.861
2d	0.713	0.747	0.865	1.619	2.874

[a] α values are given in degrees.

The proton (^1H) and carbon-13 (^{13}C) proton-decoupled NMR spectral data (100 MHz, $CDCl_3$, δ ppm downfield from Me_4Si) were as follows. ^1HNMR: (**2a**) δ 1.18 (dt, 3 H), 2.57 (qt, 1 H), 7.17 (s, 5 H); (**2b**) 1.17 (dm, 2 H), 2.57 (tm, 1 H), 7.17 (s, 5 H); (**2c**) 1.17 (dm, 1 H), 2.58 (dm, 1 H), 7.17 (s, 5 H); (**2d**) 2.58 (b s, 1 H), 7.17 (s, 5 H). ^{13}C NMR: (**2a**) δ 15.8 (s), 28.9 (t), 125.8, 127.8, 128.2, 144.3 (all s); (**2b**) 15.4 (t), 28.7 (t), 125.6, 127.8, 128.2, 144.3 (all s); (**2c**) 15.1 (quin), 28.7 (t), 125.6, 127.8, 128.2, 144.3 (all s); (**2d**) 14.8 (sept), 28.7 (t), 125.6, 127.8, 128.2, 144.3 (all s). All coupling constants (J in hertz) were as follows: J_{HH} = 8, J_{HD} = 1–2, and J_{CD} = 20.

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Registry No.—**1a**, 60208-56-2; **1a** 2,4-DNP, 68525-06-4; **1b**, 60633-85-4; **1b** 2,4-DNP, 68525-07-5; **2a**, 68566-80-3; **2b**, 68525-08-6; **2c**, 68525-09-7; **2d**, 68525-10-0; **3**, 611-71-2; **4**, 20698-91-3; **5a**, 16355-00-3; **5b**, 68525-11-1; **6a** (isomer 1), 68525-12-2; **6a** (isomer 2), 68525-13-3; **6b** (isomer 1), 68525-14-4; **6b** (isomer 2), 68525-15-5; **7a**, 33942-00-6; **7b**, 68525-16-6; **8a**, 33942-01-7; **8b**, 68525-17-7; **9a**, 68525-18-8; **10a**, 10606-76-5; **10b**, 68525-19-9.

References and Notes

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Photochemical Studies. 16.[1] Irradiation Induced Transformations of 1,2-Dihydrophthalimides and Related Compounds

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Norbornen-7-one-5,6-dicarboximides (**6a–c**) decarbonylate thermally and photochemically to the corresponding 1,2-dihydrophthalimides (**5**). The latter undergo the following wavelength and substitution dependent photochemical transformations via singlet excited states: fragmentation to benzene and benzamides (**7**), electrocyclic closure to *anti*-bicyclo[2.2.0]hex-2-ene-5,6-dicarboximides (**8**), a 1,2-acyl shift to bicyclo[3.1.0]hex-3-ene-2,6-dicarboximides (**10**), and a degenerate 1,5 shift which leaves **5** structurally unchanged. The triplet excited states, reached both by direct irradiation or sensitization, lead only to photodimers. A mechanism involving α cleavage via diradical intermediates is invoked for those photochemical processes in which the imide moiety takes active part.

We have recently embarked upon a detailed study[1,2] of the photochemical behavior of β,γ,δ,ε-unsaturated carbonyl compounds. This was spurred by our earlier findings on substituted 1,2-dihydrophthalic anhydrides[3] and imides[4] and by the recent upsurge in β,γ-unsaturated carbonyl photochemistry.[5]

After having dealt with 1,2-dihydrophthalic anhydride (**1**),[1] we wish now to report results to date of our investigation of the photochemistry of 1,2-dihydrophthalimide (**5a**) and some closely related compounds.[2]

A limited amount of information on some substituted 1,2-dihydrophthalimides was available at the start of this work. Thus, while irradiation of the 1,2,4,5-tetramethyl derivative (**5d**) had been said to cause (to an unspecified extent) electrocyclic closure accompanied by some fragmentation to durene,[6] no fragmentation was observed with the N-substituted derivatives[6] (**5e,f**) and no reaction at all with the tetraphenyl derivatives (**5g,h**).[4] On the other hand, the well delineated photochemical behavior of **1**[1] (Scheme I), fragmentation being the main and most efficient process, compelled us to examine similar systems, with the imides being first on the list.[2]

Results and Discussion

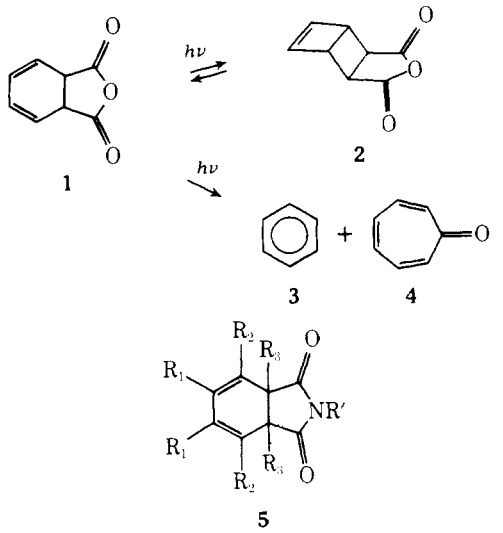
The precursors in this work were the norbornen-7-one-2,3-dicarboximides (**6**) obtained by cycloaddition of the corresponding maleimides to cyclopentadienone diethyl ketal.[1,7] Pyrolysis of **6** readily provided the 1,2-dihydrophthalimides (**5a–c**).

Exhaustive photolysis of the parent compound **5a** at 254 nm gave an unexpectedly variegated mixture of products (Scheme II), four of which were readily identified as benzene (**3**), benzamide (**7a**), *anti*-bicyclo[2.2.0]hexene-5,6-dicarboximide (**8a**), and phthalimide (**9a**). A fifth product was isolated and, following careful NMR analysis (^{1}H and ^{13}C) as elaborated below, was shown to be bicyclo[3.1.0]hex-3-ene-2,6-dicarboximide (**10a**). The respective yields at this and other wavelengths and irradiation conditions are given in Table I. The formation of an additional dimeric product was observed at higher wavelength or by sensitization and was suppressed by diene triplet quenching.

Irradiation with monochromatic light to low conversion of **5a** led to the following quantum yields for benzene formation: 0.016 (230 nm), 0.009 (257 nm) and 0.002 (284 nm). The product distribution was, in all cases, wavelength dependent as can be clearly deduced also from Tables I and II. The latter lists the yields of products from irradiation of **5c** in a variety of conditions. Furthermore, we present in Table III average yields of photoproducts obtained by irradiation of the various precursors **6** at 254 nm. We expected these data to be instructive and so they were, insofar as they showed **5** to be the key compound in the sequence leading, by further irradiation, to all other products, as depicted in Scheme II.

The efficient photodecarbonylation of **6** (e.g., $\phi_{6a}^{257} = 0.7$) resembles that of its anhydride analogue which has been discussed, and we shall not dwell on it. We focus our interest on the phototransformations of **5**. First the fragmentation processes. Using product isolation criteria alone and judging from the parallelism observed between benzene (**3**) and benzamide (**7**) yields, it is obvious that bond cleavage occurs as the primary step. One should recall that, of the scant literature on imide photochemistry, saturated imides were found

Scheme I



	a	b	c	d	e	f	g	h
R_1	H	H	H	Me	Me	Me	Ph	Ph
R_2	H	H	H	H	H	H	Ph	Ph
R_3	H	H	H	Me	Me	Me	H	H
R′	H	Et	Ph	H	C_6H_{11}	*n*-Bu	H	Ph

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