This new reaction system was successful in controlling the reactions, such that 1,5-dichloropentane and 1,6-dichlorohexane were converted to the 1,5- and 1,6-dilithio compounds, which have been previously reported by West and Rochow,[6] in identical yields of 31%.

$$ClCH_2(CH_2)_3CH_2Cl + Li_{(g)}(800\ °C) \rightarrow \underset{31\%}{LiCH_2(CH_2)_3CH_2Li} + \underset{19\%}{C_3Li_4} + \underset{11\%}{C_2Li_6} + \underset{28\%}{C_2Li_2}$$

$$ClCH_2(CH_2)_4CH_2Cl + Li_{(g)}(800\ °C) \rightarrow \underset{31\%}{LiCH_2(CH_2)_4CH_2Li} + \underset{23\%}{C_2Li_6} + \underset{19\%}{C_2Li_2}$$

However, the reactions of 1,3-dibromopropane and 1,3-dichloropropane gave completely substituted lithium compounds with no remaining protons present after hydrolysis when examined by mass spectrometry or NMR. One would conclude that the energy of the chlorine abstraction reaction was too great to dissipate prior to reaction.

$$ClCH_2CH_3CH_2Cl + Li(800\ °C) \rightarrow \underset{33\%}{CLi_3CLi_2CLi_3} + \underset{29\%}{C_2Li_6} + \underset{13\%}{CLi_2{=}CLiCLi_3}$$

The composition of the hydrolysis products which were removed from the cold finger is given in Table I. Because the only material worked up from the reaction were the products which were collected on the cold finger, the recovered material conversions in this experiment total from 25 to 35% of the theoretical and the yields are based on the material from the cold finger. The material collected on the sides of the reactor was not studied due to the difficulty of handling the entire reactor under argon.

1,5-Dichloropentane. The gas chromatographic analysis of the products from the 1,5-dichloropentane reaction showed that an *n*-pentane species was the major product, with some *n*-butane as well as several two- and three-carbon fragments (Table I). The mass spectrum of the pentane peak showed a parent ion at *m/e* 74, corresponding to $C_5H_{10}D_2^+$, and the next major peaks were at *m/e* 58 and 44, corresponding to $C_4H_8D^+$ and $C_3H_6D^+$. This pattern can arise only if the deuterium atoms are in the 1 and 5 positions, indicating that 1,5-dilithiopentane was formed. A mass spectral analysis of the remaining products showed that they were all predeuterated.

1,6-Dichlorohexane. The gas chromatographic analysis of the 1,6-dichlorohexane products gave an *n*-hexane species as the major product, with a trace of *n*-pentane, some *n*-butane, and the usual two- and three-carbon fragments. The mass spectrum of the hexane fraction was interpreted (by the same process used on pentane) as indicating that this material was 1,6-dideuteriohexane. The pentane was found to be 1,5-dideuteriopentane, and the butane was found to be a mixture of species with 2–10 deuteriums present. The other products were predeuterated and, therefore, likely to be produced by a fragmentation process.

1,3-Dichloro- and 1,3-Dibromopropanes. The 1,3-dibromopropane reaction gave a propene species as the major product with a propane to propene ratio of 1:3.4; the 1,3-dichloropropane reaction gave a propane species as the major product with a propane to propene ratio of 2.7:1. A mass spectrum of the propane products showed, in both cases, that the propane was predeuterated, with no trace of the desired 1,3-dideuteriopropane.

As previously mentioned in the manuscript, West and Rochow have studied the reactions of dibromoalkanes with lithium metal in ethyl ether and have previously prepared the compounds 1,5-dilithiopentane and 1,6-dilithiohexane.[6] Very interestingly, in a series of six α,ζ-dibromoalkanes, only $Br(CH_2)_2Br$ and $Br(CH_2)_3Br$ have been reported to yield no dilithio products. In this study the lithium compound was quenched in situ with chlorotrimethylsilane. While the reaction was reported to work well for the methylene analogue and higher analogues with yields as high as 71% of the trimethylsilyl derivative obtained, West and Rochow reported that absolutely none of the trimethysilyl compounds were obtained for the ethyl and propyl analogues and that only a small amount of a rather involatile oil was left after distillation.

Registry No.—1,5-Dichloropentane, 628-76-2; 1,6-dichlorohexane, 2163-00-0; 1,3-dichloropropane, 142-28-9; 1,3-dibromopropane, 109-64-8; $LiCH_2(CH_2)_3CH_2Li$, 2223-58-7; C_3Li_4, 69815-14-1; C_2Li_6, 38827-80-4; C_2Li_2, 1070-75-3; $LiCH_2(CH_2)_4CH_2Li$, 2223-57-6; $CLi_3CLi_2CLi_3$, 69815-15-2; $CLi_2{=}CLiCLi_3$, 69815-16-3.

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Absolute Configuration of Chalcone Epoxide. Chemical Correlation

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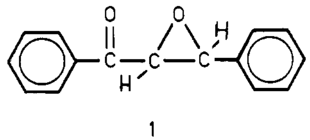
The chiral epoxychalcone 1 is one of a series of optically active epoxy ketones recently prepared via asymmetric catalysis.[1a–c] Crucial in an understanding of the mechanism of this asymmetric synthesis is the knowledge of the absolute configuration of the chiral product. Assignment of absolute configuration using the sign of the Cotton effect is unreliable in the case of 1 and its homologues since the absolute conformation is unknown. Determination of the absolute configuration by X-ray structure determination of a series of epoxy ketones has obvious inherent difficulties. The correlation of the absolute configuration of 1 described in this paper can without undue difficulty be applied to other epoxychalcones carrying like or unlike substituents in either ring.



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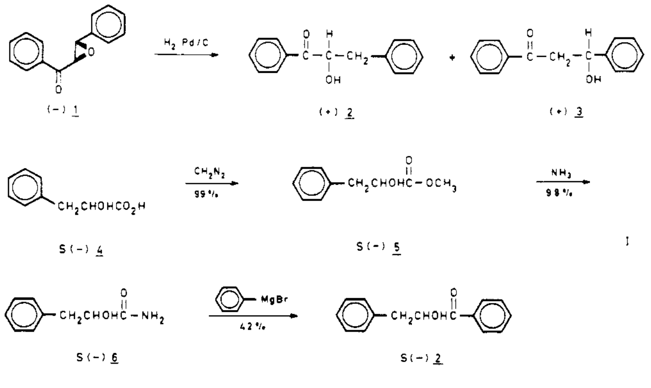
Scheme I shows the chemical correlation used. Reduction

Scheme I



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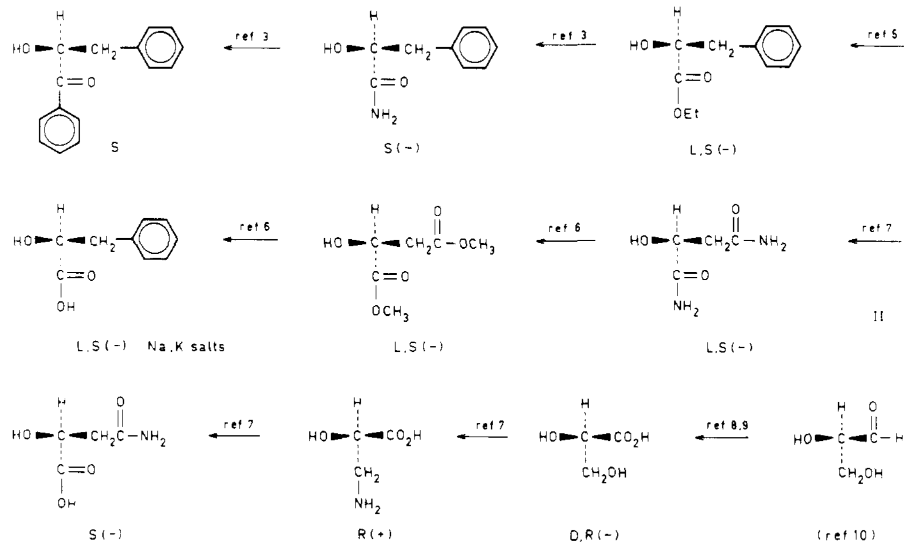
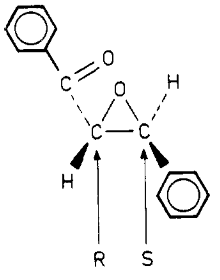
Scheme II



of optically active epoxychalcone 1 ([α]$_{578}$ −65 (CH_2Cl_2); 31 ± 5%; see ref 1 for preparation and enantiomeric purity which was determined with the aid of Eu(dcm)$_3$) with palladium on charcoal in ethanol reported[2] to give 2-hydroxy-3-phenylpropiophenone (2) in our hands furnished in 40% yield a mixture containing 90% of (+)-2 and 10% (+)-3.

The mixture could be separated using LC, and chemically pure 2 ([α]$_{578}$ +3.8 acetone) and 3 ([α]$_{578}$ +18) could be isolated and identified. We obtained (−)-2 from commercially available L(−)-α-phenyllactic acid with [α]$_{589}$ = −13 (*c* 1.04 acetone). This rotation agrees well with that reported by MacKenzie[3] for (+)-2, with [α]$_{589}$ +12.6 (acetone). Kagan[4] has correlated the hydroxy ketone (−)-2 of MacKenzie with compounds of known configuration and has determined the *S* configuration for (−)-2 (see Scheme II).

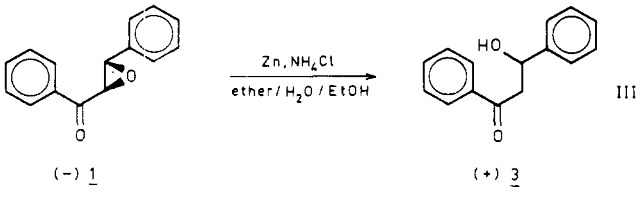
We conclude that the configuration of (+)-2 is *R*. Based on the fact that the enantiomeric excess of (−)-1 and the optical purity of (+)-2 are of similar magnitude, we assume that the configuration of the carbon α to the ketone does not change during the reduction. Thus (−)-1 has the *R* configuration on the carbon α to the ketone. The carbon β to the ketone function must have the *S* configuration since (−)-1 is a trans epoxy ketone.



(−) 1

We also carried out a reduction of (−)-1 with zinc dust. This gave exclusively the β-hydroxy ketone (+)-3 (Scheme III). We found (+)-3 with [α]$_{578}$ +20 (*c* 0.65, CH_2Cl_2) which was similar to that of (+)-3, formed in Scheme I. This reduction apparently does not give racemization on the carbon β to the ketone function. To our knowledge, 3 has not been prepared in optically active form before. The absolute configuration of (+)-3 is *S*, since we can correlate (+)-3 with (−)-1 (see Schemes I and III).

Scheme III



The CD spectra of (−)-1 and (−)-2 were also obtained: (−)-1 measured in methanol gives a negative Cotton effect (CE) for the n–π^* transition with an extremum at λ 322 nm ($\Delta\epsilon$ −2.864). The π–π^* transition shows a negative extremum at λ +257 nm ($\Delta\epsilon$ −6.301) and a positive extremum at λ 235 nm ($\Delta\epsilon$ +8.306). When the spectra of (−)-2 were measured in hexane, in order to enhance intramolecular hydrogen bonding, a positive CE for the n–π^* transition was obtained with a maximum at λ 305 ($\Delta\epsilon$ +0.652) and a negative CE for the π–π^* transition with an extremum at λ 278 nm ($\Delta\epsilon$ −1.386).

Experimental Section

Chalcone Epoxide [(−)-1]. To a solution of 10.4 g (50 mmol) of chalcone and 0.5 g of quininiumbenzyl chloride[11] in 70 mL of carbon tetrachloride was added a mixture containing 35 mL of a 30% H_2O_2 solution and 35 mL of a 12% NaOH solution. After the solution was stirred for 100 h at 3 °C, CH_2Cl_2 was added to dissolve the solid material that was present in the reaction mixture. The organic layer was separated from the water layer and extracted 5× with 50 mL of H_2O. After the layer was dried ($MgSO_4$), the solvent was evaporated, and 10.1 g of chalcone epoxide (92%) was obtained. The quininiumbenzyl chloride was completely removed by column chromatography over silica gel with CH_2Cl_2 as eluent. ^1H NMR data were identical with those reported in the literature:[2] [α]$^{rt}_{578}$ −72.2° (*c* 0.69, CH_2Cl_2); optical purity 34%; mp 82–84 °C (mp (±) 90 °C).

3-Hydroxy-3-phenylpropiophenone [(+)-3]. To a solution of 1 g of chalcone epoxide ([α]$^{rt}_{578}$ −69°) in a mixture of 25 mL of ether, 35 mL of ethanol, and 12 mL of H_2O was added 1 g of NH_4Cl and 3 g of zinc dust. After the mixture was stirred for 17 h at room temperature, solid material was removed by filtration and the filtrate was partially evaporated. Ether and water were added to the mixture, and after acidification of the mixture the organic layer was washed with 3 × 20 mL of water and 1 × 20 mL of a saturated NaCl solution. After the solution was dried ($MGSO_4$), the solvent was removed, and the residue contained the crude product (0.75 g). Purification of the product was carried out by thick-layer chromatography (silica gel/CH_2Cl_2) resulting in 0.58 g of pure 3-hydroxy-3-phenylpropiophenone (58%): [α]$^{rt}_{578}$ +20° (*c* 0.65, CH_2Cl_2); ^1H NMR was identical with that reported in ref 12; IR (Nujol) 1680, 1670 (C=O), and 3600 (OH) cm^{-1}.

2-Hydroxy-3-phenylpropiophenone [(+)-2]. Chalcone epoxide (1 g) ([α]$^{rt}_{578}$ −65) on 100 mL of ethanol containing 0.1 g of Pd–C (5%) was hydrogenated for half an hour at 1 atm in a Parr low-pressure hydrogenator. After filtering, evaporating, and drying ($MgSO_4$) the solution, the product was purified by thick layer chromatography (silica gel, CH_2Cl_2) giving 0.4 g of a mixture containing ca. 90% of 2-

hydroxy-3-phenylpropiophenone [(+)-**2**] and ca. 10% of 3-hydroxy-3-phenylpropriophenone [(+)-3] which were separated by LC (30 cm. ⅜ in. o.d., Lichrosorb Si 60, 5 μm/CH_2Cl_2). (+)-**3** ($[\alpha]^{rt}_{578}$ +18° (CH_2Cl_2)) gave spectral data as above. (+)-**2** gave: ^1H NMR ($CDCl_3$) δ 7.9–6.9 (10 H), 5.2 (m, 1 H), 3.6 (d, OH), 3.3–2.6 (m, 2 H); IR (Nujol) 1760 (C=O) and 3500 (OH) cm^{-1}; $[\alpha]^{rt}_{589}$ +3.8° (*c* 0.58, acetone).

Methyl Ester of L(−)-β-Phenyllactic Acid^{13} [(−)-5]. To a solution of 0.83 g (5 mmol) of L(−)-β-phenyllactic acid in 25 mL of ether was added at 0 °C 1 equiv of a diazomethane solution in ether. The solvent was evaporated resulting in 0.89 g (99%) of (−)-**5**: ^1H NMR ($CDCl_3$) δ 7.3–7.1 (5 H), 4.5–4.2 (m, 1 H), 3.7 (s, 3 H), 3.0 (m, 2 H), 1.8–1.6 (d, OH); IR (Nujol) 1745, 1730 (C=O), and 3400–3200 (OH) cm^{-1}; $[\alpha]^{rt}_{578}$ −15.3° (*c* 0.62, CH_2Cl_2).

L(−)-β-Phenyllactamide [(−)-6]. To a solution of 2.9 g (16 mmol) of (−)-**5** in 10 mL of methanol was added an excess of liquid ammonia. After the solution stood for a week at room temperature, 2.6 g (15.7 mmol) of product was obtained by evaporating the solvent and the ammonia: yield 98%; mp 109–112 °C; ^1H NMR ($CDCl_3$) δ 7.4–7.2 (5 H), 4.5–4.2 (m, 1 H), 3.1 (m, 2 H), 2.0 (br, s, NH_2); IR (Nujol) 1685 (C=O), and 3500–3200 (OH) cm^{-1}; $[\alpha]^{rt}_{578}$ −85.0° (*c* 1.24, EtOH).

L(−)-2-Hydroxy-3-phenylpropiophenone [(−)-2]. To a refluxing suspension of 0.38 g of activated Mg and an I_2 crystal in 10 mL of ether was added a solution of 2.4 g of bromobenzene in 5 mL of ether. After the reaction had started, refluxing was continued for half an hour. This mixture was added to a solution of 0.5 g of (−)-**6** in ether. After the solution was refluxed for 6 h, 20 mL of a saturated NH_4Cl solution was added, the mixture was acidified, and the organic layer was extracted with 3 × 20 ml of water and 1 × 20 mL of a saturated NaCl solution. After the solution was dried ($MgSO_4$) and the solvent removed, 0.56 g of crude product was obtained. Purification by thick-layer chromatography (silica gel/CH_2Cl_2) gave 0.28 g of (−)-**2** (42%): mp 50–52 °C; ^1H NMR ($CDCl_3$) δ 7.9–6.9 (10 H), 5.2 (m, 1 H), 3.6 (d, OH), 3.3–2.6 (m, 2 H); IR (Nujol) 1670 (C=O) and 3500 (OH) cm^{-1}; $[\alpha]_{589}^{rt}$ −13° (*c* 0.14, acetone).

Registry No.—(−)-**1**, 61840-92-4; (+)-**2**, 69897-44-5; (−)-**2**, 69897-45-6; (+)-**3**, 69897-46-7; (−)-**4**, 20312-36-1; (−)-**5**, 13673-95-5; (−)-**6**, 69897-47-8; chalcone, 94-41-7; bromobenzene, 108-86-1.

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Electron-Transfer Processes: Oxidation of Naphthalene and *p*-Cymene by Peroxydisulfate

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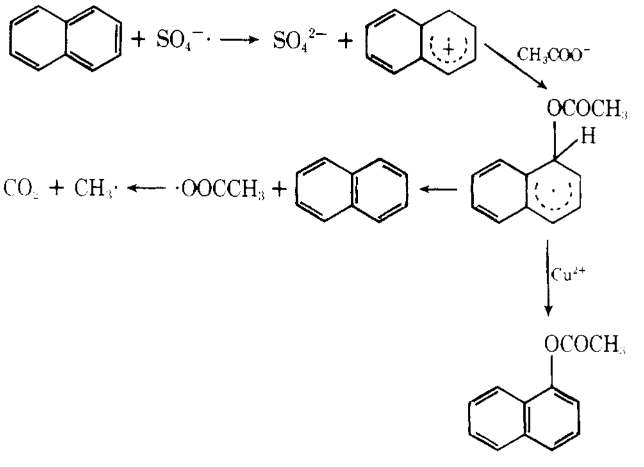
A recent report[1] shows that the oxidative acetoxylation of aromatic compounds by Ag(II) complexes in acetic acid can be made catalytic in the presence of an excess of peroxydisulfate, but no acetoxylation takes place in the absence of silver salt and in the presence of Cu(II) salts. We have found that direct aromatic acetoxylation of naphthalene by peroxydisulfate (Scheme I) occurs also in the absence of silver salt and in the presence of Cu(II) salts.

Scheme I



Under similar conditions in the presence of Fe(III) salts, no acetoxylation takes place, but α-(hydroxymethyl)naphthalene acetate (1) is obtained as the main reaction product of naphthalene.

p-Cymene gives *p*-isopropylbenzyl acetate (2) by copper-catalyzed oxidation under the same conditions.

The oxidation of *p*-cymene with peroxydisulfate in the presence of *p*-benzoquinone gives the 2-(*p*-isopropylbenzyl)benzoquinone in 40% yield; moreover, *p*-isopropylbenzyl alcohol and *p*-isopropylbenzaldehyde have been formed in an additional 30% yield.

These results provide further evidence concerning the formation of aromatic radical cations in the interaction of the sulfate radical anion, $SO_4^{-}\cdot$, with aromatics.[2–7] The absence of acetoxynaphthalene in the absence of Cu(II) salts could be explained by the competitive routes of Scheme I.

The formation of 1 could arise from the oxidation by $S_2O_8^{2-}$ of methylnaphthalene or of naphthylacetic acid, formed in situ from naphthalene and $CH_3\cdot$, and from naphthalene and $\cdot CH_2COOH$, respectively. The presence of both methyl and $\cdot CH_2COOH$ radicals in the reaction medium has been evidenced by trapping these radicals with quinoxaline or styrene under the reaction conditions.[8] Methylquinoxaline and γ-phenylbutyrolactone[9] have been identified among the reaction products.

Experimental Section

Acetoxynaphthalenes. Potassium peroxydisulfate (0.01 mol) was added to a well-stirred solution of $Cu(OAc)_2$ (0.02 mol), KOAc (0.04 mol), and naphthalene (0.02 mol) in acetic acid (50 mL) at 113 °C under a nitrogen atmosphere. The reaction mixture was stirred at 113 °C for 5 h. An internal standard was added to the reaction mixture, which was then extracted with ether and water. The organic layer was dried and analyzed by GLC. The acetoxynaphthalenes (α/β = 93:7) were identified by comparison with authentic samples (GLC, IR, MS). The yield based on converted naphthalene was 90%. The yield based on peroxydisulfate was 39%.

***α*-(Hydroxymethyl)naphthalene Acetate.** The procedure was identical with that utilized for acetoxynaphthalenes with the only difference being that basic ferric acetate (0.005 mol) was used instead of cupric acetate and the reaction mixture was refluxed for 6 h. GLC revealed the presence of α-(hydroxymethyl)naphthalene acetate, identified by comparison with an authentic sample. The yield based on converted naphthalene was 60%; the yield based on peroxydisulfate was 18%.

***p*-Isopropylbenzyl Acetate.** Starting from *p*-cymene, the copper-catalyzed procedure was identical with that used for naphthalene. Conversion of *p*-cymene was 32%; the yield based on converted *p*-cymene was 70%: NMR δ 1.05 (d, 6 H), 2.05 (s, 3 H), 2.75 (m, 1 H), 5.03

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