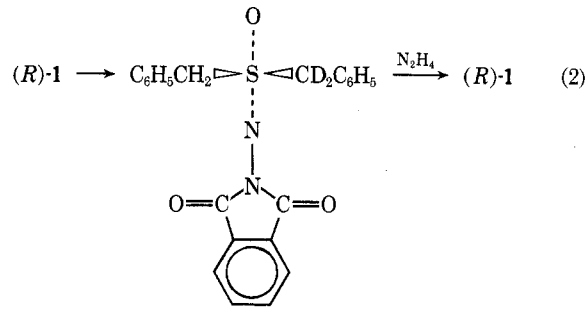
strength in (−)-(*S*)-[4-^{2}H][2.2]paracyclophane via a similar vibronic coupling mechanism.[6,12]

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

Table I
Relative Reactivities of Aromatics toward Undecyl Radicals at 81°

Registry no.	Compd	Relative reactivity[a]
104-85-8	*p*-Cyanotoluene	2.03 ± 0.02
100-47-0	Benzonitrile	1.78 ± 0.02
620-22-4	*m*-Cyanotoluene	1.66 ± 0.02
108-41-8	*m*-Chlorotoluene	1.24 ± 0.03
104-93-8	*p*-Methoxytolutne	1.24 ± 0.01
352-70-5	*m*-Fluorotoluene	1.16 ± 0.03
100-84-5	*m*-Methoxytoluene	1.12 ± 0.01
106-43-4	*p*-Cholorotoluene	1.09 ± 0.01
352-32-9	*p*-Fluorotoluene	1.04 ± 0.03
108-88-3	Toluene	1.00[b]
108-38-3	*m*-Xylene	0.97 ± 0.01[c]
106-42-3	*p*-Xylene	0.89 ± 0.02[c]
108-90-7	Chlorobenzene	0.72 ± 0.01
100-66-3	Anisole	0.45 ± 0.04

[a] Against toluene; each entry represents the results of at least two runs, each analyzed in triplicate. [b] Assigned. [c] Normalized.

only 14% greater than that of benzonitrile, an indication of preponderance of addition over benzyl hydrogen abstraction for this toluene. *p*-Chlorotoluene is 50% more reactive than chlorobenzene, indicating that addition and benzyl hydrogen abstraction are roughly comparable in this case. *p*-Methoxytoluene is 270% more reactive than anisole, indicating that benzyl hydrogen abstraction is predominant for this toluene.

A study of all the data in Table I supports the inferences that (1) electron-withdrawing groups on the aromatic nucleus increase the rate of addition by undecyl radicals, and (2) electron-donating groups increase the rate of benzyl hydrogen abstraction. The first inference is in agreement with the conclusions of Shelton and Uzelmeir on additions of secondary alkyl radicals to substituted benzenes,[8] and the second with our predictions regarding abstractions by alkyl radicals.[2]

Our analyses indicate that the amount of undecane obtained exceeds the combined amounts of toluenes reacted, in all cases, often by as much as 25%. The stoichiometry of alkane formation following addition is not clear enough to warrant any additional quantitative conclusions. However, it is well known that methane-*d* is one of the products of the reaction of methyl radicals with ring-deuterated toluene.[9]

A serious discrepancy exists between the value of relative reactivity for *p*-methoxytoluene determined by us (1.24 by GLC) and that of Pryor et al.[5] (0.69 by NMR of the benzylic CH_3).

If the data for *p*-methoxytoluene and for the benzenes are disregarded (Table I), a Hammett plot of *total* reactivity for the remaining toluenes gives $\rho = 0.4$, with tolerable scatter. This is near the value of 0.47 reported by Henderson and Ward,[4] and 0.50 by Pryor and Davis;[5] both groups have described their Hammett plots as reflecting benzylic hydrogen abstraction exclusively.[10]

It must be pointed out that our results can support only tentative interpretations at this point. Kinetic studies, such as this and similar ones,[3-6] without fairly complete mass balance, should be interpreted with care.[11]

Experimental Section

Relative reactivities were determined by direct competition against toluene. Each toluene or substituted benzene was made approximately 0.67 *M* in benzene and brought to a gentle reflux; a solution of lauroyl peroxide in benzene was added over a 15-min period to a final concentration of 0.47 *M*. Reflux was continued for 36 hr. A blank (no peroxide) was treated in the same way. Each experiment was performed at least twice. Analyses were performed by GLC in triplicate; *p*-dichlorobenzene was added at the completion of the reaction as an internal standard.

Registry No.—Undecyl radical, 55101-35-4.

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Reaction of Ketene Bis(trimethylsilyl) Acetals with *m*-Chloroperbenzoic Acid. Synthesis of α-Hydroxycarboxylic Acids

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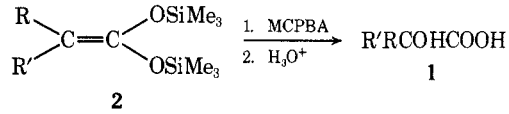
Available methods for the preparation of α-hydroxycarboxylic acids, **1**, include the aeration of lithiated carboxylic acids,[1] the hydrolysis of α-acyloxycarboxylic acids,[2] and the Favorski reaction.[3] Recently, also syntheses of **1** via trihalomethylcarbinols[4] and by use of the Pummerer reaction[5] have been noted.

We should like to report here that the oxidation of ketene bis(trimethylsilyl) acetals, **2**, with *m*-chloroperbenzoic acid (MCPBA), followed by mild acid hydrolysis, affords an extremely general, high-yield method for the preparation of **1** (Scheme I). The data included in Table I indicate the utility of the method.

Scheme I



2 **1**

The mode of reaction of **2** with MCPBA may be envisioned as shown in Scheme II. This mechanistic route follows closely the scheme proposed for the reaction of trimethylsilyl enol ethers with MCPBA.[6] The presence of **5b** in the reaction mixture obtained from treating **2b** with MCPBA, prior to hydrolysis, was ascertained by direct distillation of the crude reaction mixture. Despite a great deal of decomposition, a 32% yield of **5b** was obtained. The structure of **5b** was verified by NMR and mass spectral comparison with authentic **5b**. The low yield of **5b** obtained by this procedure makes mechanistic considerations somewhat tenuous, but, based on analogy,[6] a [1,4]silatropic shift accounting for the production of **5b** seems to best fit the data.[6,7] No evidence for the presence of **3** was noted, but, in