Stereochemistry of Free-Radical Recombination Reactions. The Cage Effect in Decomposition of *S*-(+)-*tert*-Butyl 2-Phenylperpropionate[1]

JON P. ENGSTROM AND FREDERICK D. GREENE*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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Decomposition of *tert*-butyl 2-phenylperpropionate in cumene at 60° in the presence of butanethiol scavenger afforded a 10% yield of *tert*-butyl 1-phenylethyl ether. The cage effect, measured by use of the Koelsch radical, was 42%. The decomposition of optically active perester, *S*-(+)-*tert*-butyl 2-phenylperpropionate, in the presence of 0.5 *M* butanethiol gave *tert*-butyl 1-phenylethyl ether with 20% net retention of configuration. The absolute configuration and maximum rotation of the ether have been determined independently; (−)-ether is of *S* configuration. The principal result of this study is that the rate of 180° out-of-plane rotation of the 1-phenylethyl radical with respect to the *tert*-butoxyl radical within the solvent cage (Scheme I) is approximately 4.5 times as fast as the rate of the cage termination reactions (combination plus disproportionation).

Stereospecific radical reactions may be separated into several groups. One group is composed of reactions that are stereospecific because the radical can maintain configuration long enough to undergo an atom transfer or an electron transfer reaction before inverting. Examples of this type of stereospecific reaction are the reduction of 7-halo-7-fluoronorcaranes[2] and the reduction of 3-bromo-3-hexenes with sodium naphthalide.[3] Decomposition of *tert*-butyl 9-decalylpercarboxylate in the presence of a high concentration of oxygen[4] and decomposition of 9-decalylcarbinyl hypochlorite[5] may also be examples of this type, or may be of a different type in which the stereospecificity is associated with atom transfer to a (planar) radical at a faster rate than conformational changes elsewhere in the system. A third group is composed of reactions that are stereospecific because the radical has a reactive partner initially positioned in a stereospecific manner within the solvent cage; examples of this latter category are cyclic azo decomposition (pyrazolines[6] and tetrahydropyridazines[7]), cage combination,[8,9] cage disproportionation,[10] photobromination,[11] and probably a number of oxidation reactions[12a,b] and rearrangement reactions[12c] of ylides and carbanions. Stereospecificity in this class of reactions does not require that the radical maintain configuration. As has been pointed out for cage combination reactions,[9] the caged arrangement is asymmetric and may give rise to stereospecific products even for cages in which the radicals may be planar. Although cage combination reactions are limited in the information about radical structure, they permit certain insights into the nature of cage reactions.

Stereochemical studies of free radical cage reactions represent an approach to detailed information on the behavior of molecules in media over a wide range of viscosity. Two recent studies on azo decompositions[8,9] have elucidated the degree of freedom of a radical pair derived from an optically active azo compound. Homolytic perester decomposition may generate an alkyl radical, an alkoxyl radical, and a carbon dioxide molecule within the solvent cage.[13,14] Several important factors distinguish the cage resulting from perester decomposition from the cage resulting from azo compound decomposition. First, the perester cage contains an alkoxyl radical that is quite reactive as a hydrogen abstracting agent. Second, the alkoxyl radical and the alkyl radical are on atoms of different electronegativity and may be influenced by polar contributions.[13e,15] Third, a molecule of carbon dioxide rather than nitrogen initially separates the two radicals.

In this paper we describe the decomposition of *tert*-butyl 2-phenylperpropionate and provide information on the relative rates of the cage reactions.

Results

Products.—*tert*-Butyl 2-phenylperpropionate (**1**) decomposes in cumene to give a 1-phenylethyl radical, carbon dioxide, and a *tert*-butoxyl radical. The products in the absence of scavenger are given in Table I. The products are analogous to those formed in the decomposition of *tert*-butyl 2-phenylperisobutyrate.[14] The low accounting for the 1-phenylethyl groups (64%) is thought to result from polymerization of some of the styrene. Studies on the cage effect (see below) suggest that styrene is formed in 30% yield within the solvent cage.

Cage Effect.—The magnitude of the cage effect was determined by the "excess initiator" method[16] using the Koelsch radical.[17] In this method the rate

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[1] Financial support from the Atomic Energy Commission [Contract No. AT(30-1)-905] is gratefully acknowledged.

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TABLE I

PRODUCTS FROM THE DECOMPOSITION OF *tert*-BUTYL 1-PHENYLPERPROPIONATE (1) IN CUMENE AT 60° IN THE ABSENCE OF SCAVENGER

Product	Yield, %[a]
$C_6H_5CH(CH_3)OC(CH_3)_3$	16
$C_6H_5CH{=}CH_2$	(5)
$C_6H_5C_2H_5$	5
$PhCH(CH_3)CH(CH_3)Ph$[b]	12
$PhC(CH_3)_2CH(CH_3)Ph$	14
$(CH_3)_3COH$	74
$PhC(CH_3)_2C(CH_3)_2Ph$	~10

[a] The total percentage of alkyl groups accounted for is 64%; the total percentage of *tert*-butyl groups accounted for is 90%. [b] Both meso and *dl* isomers were present in approximately 1:1 ratio.

of radical production is determined during the first 1–5% of the decomposition; the scavenging experiments thus could be carried out at lower temperatures than for the "excess scavenger" method,[18] and the problem of scavenged product instability was circumvented. The excess initiator method depends upon measuring the difference in the rate of initiator disappearance and the rate of radical production.

The rate of decomposition of *tert*-butyl 2-phenylperpropionate in cumene was determined by following the rate of disappearance of the carbonyl absorption in the infrared spectrum at 1770 cm^{-1}. A summary of the rate constants appears in Table II. The enthalpy of activation for decomposition is 25.5 kcal/mol and the entropy of activation at 60° is −0.1 eu.

TABLE II

DECOMPOSITION OF *tert*-BUTYL 2-PHENYLPERPROPIONATE IN CUMENE

Temp, °C	k, sec^{-1}
40.7	7.60×10^{-6}
40.7	8.16×10^{-6}
60.1	8.38×10^{-5}
60.1	8.49×10^{-5}
80.1	8.10×10^{-4}

The rate of radical formation was followed by observing the decrease in the scavenger absorption[16] in the visible spectrum. The decrease in scavenger concentration with time was linear in all cases, affording the zero-order rate constants, λ. The cage effect, F, defined in the usual manner (eq 1), was calculated by eq 2, in which k_1 is the rate constant for decomposition

$$F = \left(\frac{k_{\text{combination}} + k_{\text{disproportionation}}}{k_{\text{combination}} + k_{\text{disproportionation}} + k_{\text{diffusion}}}\right)_{\text{cage}} \qquad (1)$$

$$F = 1 - \frac{\lambda}{2k_1[\text{perester}]_0} \qquad (2)$$

of the perester and in which the factor 2 appears in the denominator because of the maximum generation of two radicals for every perester molecule undergoing decomposition. The results are summarized in Table III. An estimate for the cage effect at 60° of 0.42 ± 0.03 was obtained by extrapolation of the data of Table III.[19]

TABLE III

DETERMINATION OF CAGE EFFECT BY CONSUMPTION OF KOELSCH RADICAL[a] IN THE DECOMPOSITION OF *tert*-BUTYL 2-PHENYLPERPROPIONATE (I)[b] IN CUMENE

Temp, °C	$(\lambda/P_0) \times 10^6$,[c] sec^{-1}	$k_1 \times 10^6$,[d] sec^{-1}	Cage effect, F[e]
30.1	1.43	1.87[b]	0.62 ± 0.03
40.5	6.78	7.7	0.56 ± 0.03
48.3	20.4	21.0[f]	0.51 ± 0.03
60.1	97.8[g]	84.4	0.42

[a] Initial concentration, ~1×10^{-4} M (~1% of perester concentration). [b] Range of initial concentrations, 0.01–0.025 M. [c] Zero-order rate constant for disappearance of Koelsch radical = λ. [d] Rate of decomposition of perester (see Table II). [e] Calculated by eq 2. [f] Extrapolated; see Table II. [g] Extrapolated value from the data at 30.1, 40.5, and 48.3° by means of a linear plot of log (λ/P_0) *vs.* $1/T$.

The amount of *tert*-butyl 1-phenylethyl ether formed within the solvent cage was determined by decomposing the perester in the presence of varying concentrations of butanethiol. The yield of ether decreases with increasing butanethiol concentration until the concentration of butanethiol reaches 0.1 M and then remains constant at 10% (see Table IV). At concentrations of butanethiol greater than 0.10 M it was assumed that all the radicals escaping the solvent cage were scavenged and did not give *tert*-butyl 1-phenylethyl ether.

TABLE IV

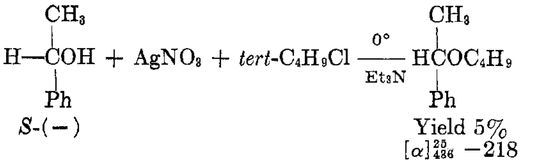
DECOMPOSITION OF *tert*-BUTYL 2-PHENYLPERPROPIONATE[a] IN CUMENE IN THE PRESENCE OF BUTANETHIOL AT 60°

n-BuSH, M	Yield of ether, %
0	16.5
0.005	15.3
0.010	12.9
0.05	11.0
0.10	9.8
0.50	9.9

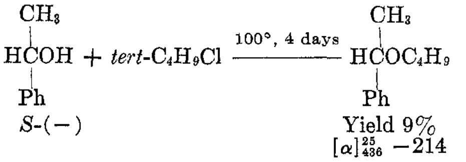
[a] Initial concentration, 0.025 M.

Optically Active 1.—*S*-(+)-*tert*-Butyl 2-phenylperpropionate was prepared according to standard procedures from *S*-(+)-2-phenylpropionic acid. Reduction of the perester with potassium iodide and acetic acid afforded the starting acid with greater than 98% retention of optical activity.

S-(−)-*tert*-Butyl 1-phenylethyl ether was prepared from *S*-(−)-1-phenylethanol by the methods given in eq 3 and 4.



$$\underset{S\text{-}(-)}{\text{H—}\overset{\text{CH}_3}{\underset{\text{Ph}}{\text{C}}}\text{OH}} + \text{AgNO}_3 + tert\text{-C}_4\text{H}_9\text{Cl} \xrightarrow[\text{Et}_3\text{N}]{0^\circ} \underset{\substack{\text{Yield } 5\% \\ [\alpha]^{25}_{436}\ -218}}{\text{H}\overset{\text{CH}_3}{\underset{\text{Ph}}{\text{C}}}\text{OC}_4\text{H}_9} \qquad (3)$$



$$\underset{S\text{-}(-)}{\text{H}\overset{\text{CH}_3}{\underset{\text{Ph}}{\text{C}}}\text{OH}} + tert\text{-C}_4\text{H}_9\text{Cl} \xrightarrow{100^\circ,\ 4\text{ days}} \underset{\substack{\text{Yield } 9\% \\ [\alpha]^{25}_{436}\ -214}}{\text{H}\overset{\text{CH}_3}{\underset{\text{Ph}}{\text{C}}}\text{OC}_4\text{H}_9} \qquad (4)$$

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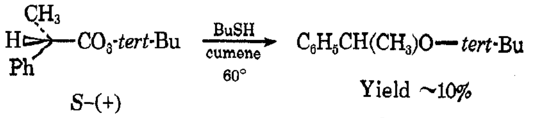
to use the "excess scavenger" method failed, presumably because the scavenged products were unstable. (c) R. Kuhn and F. A. Neugebauer, *Monatsh. Chem.*, **95**, 3 (1964). (d) For evidence on the efficiency of the Koelsch radical as a scavenger for cumyl radical, see ref 17b.

(18) R. C. Lamb and J. G. Pacifici, *J. Amer. Chem. Soc.*, **86**, 914 (1964).

(19) A linear plot of log (λ/P_0) *vs.* $1/T$ was used for the extrapolation. For related problems, see *tert*-butyl 2-phenylperisobutyrate (ref 15) and azo decompositions [L. Herk, M. Feld, and M. Szwarc, *J. Amer. Chem. Soc.*, **83**, 2998 (1961)].

S-(+)-*tert*-Butyl 2-phenylperpropionate was decomposed in cumene in the presence of butanethiol (0.50 *M*) at 60°, *i.e.*, under conditions of complete scavenging of all radicals escaping the solvent cage (see above). After ten half-lives *tert*-butyl 1-phenylethyl ether was isolated. The degree of retention of optical activity in the ether from three different experiments is given in eq 5.



(5)

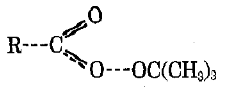
Yield ~10%

S-(−)[a]	*R*-(+)
60.3	39.7
60.9	39.1
59.9	40.1

[a] Corresponds to retention of configuration in this reaction.

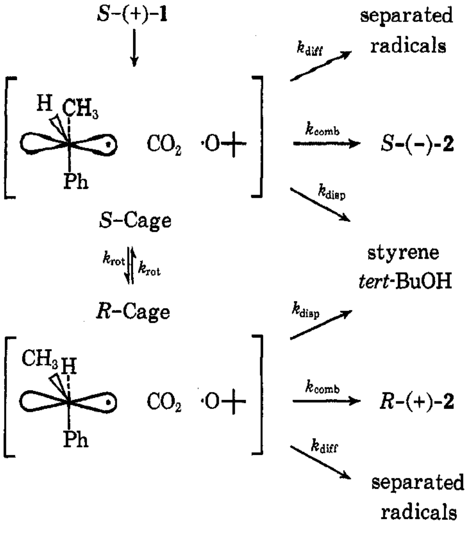
Discussion

Several lines of evidence (isotope effects,[13c] effect of viscosity[13d] and pressure[13e] on rate, and activation parameter comparisons[13a]) from a number of peresters are suggestive that the rate-determining step for decomposition of *tert*-butyl 2-phenylperpropionate (**1**) will involve two-bond cleavage affording 1-phenylethyl radical, carbon dioxide, and *tert*-butoxyl radical. The probable geometry for the transition state is one in which the incipient alkyl and alkoxyl radicals are trans to one another with respect to the developing carbon–oxygen double bond, giving rise to a caged pair of radicals initially separated by a molecule of carbon dioxide. The subsequent reactions—cage combination



and disproportionation, rotation, and diffusion—are dependent on the relative rates of diffusive displacements of the radicals, carbon dioxide, and the surrounding solvent molecules. Interpretation of the results of the decomposition of optically active perester **1** is based on Scheme I. The situation is closely analogous to the decomposition of *S*-(−)-1,1′-diphenyl-1-methylazomethane.[8]

SCHEME I



In the analysis of Scheme I, the rate constants for diffusion (k_{diff}), combination (k_{comb}),[20] and disproportionation (k_{disp})[20] are assumed to be the same for both cages. The rate constant, k_{rot}, refers to a 180° out-of-plane rotation of the 1-phenylethyl radical relative to the *tert*-butoxyl radical, and is also assumed to be the same for both cages.

By the usual steady-state approximation (working with $-\text{d}[R_{\text{cage}}]/\text{d}t \cong 0$, Scheme I, and with $\text{d}[R\text{-}2]/\text{d}t$ and $\text{d}[S\text{-}2]/\text{d}t$), the optical activity of the ether cage product may be expressed in terms of the rate constants (eq 6). By use of the definition of eq 7, eq 6 may be reexpressed as eq 8. In terms of this analysis, the mole fraction of ether formed in the original solvent cages (*i.e.*, the yield of ether under scavenging conditions) and the optical activity of this ether provide a measure of the ratio of $k_{\text{comb}}/k_{\text{rot}}$. One sees that this value is not dependent on the value of the cage effect[21] or on the amount of cage recombination.

$$\frac{S\text{-}2 - R\text{-}2}{R\text{-}2} = \frac{k_{\text{diff}} + k_{\text{comb}} + k_{\text{disp}}}{k_{\text{rot}}} \tag{6}$$

$$\text{mf } 2 = \text{mole fraction of ether formed in the cage} = \frac{k_{\text{comb}}}{(k_{\text{diff}} + k_{\text{comb}} + k_{\text{disp}})} \tag{7}$$

$$\frac{k_{\text{comb}}}{k_{\text{rot}}} = \frac{S\text{-}2 - R\text{-}2}{R\text{-}2}(\text{mf } 2) \tag{8}$$

By means of eq 1, eq 9, and the value for F at 60° of 0.42 (Table III), the relative values of the rate constants may be estimated.[22] (The relative value for k_{disp} is thus obtained as the difference between total cage reaction and the amount of cage ether.) These values are summarized in Table V along with values from some related studies of azo decompositions. The ratio of disproportionation to combination is considerably greater with perester **1** than with the second and third entries of Table V. The implication that disproportionation is faster for an alkyl–alkoxyl radical pair than for an alkyl–alkyl pair is not surprising based on the knowledge that hydrogen abstraction by an alkoxyl radical is generally faster than abstraction by an alkyl radical.

$$\frac{k_{\text{comb}}}{k_{\text{comb}} + k_{\text{disp}}} = \frac{0.1}{0.42} \tag{9}$$

A question of primary interest in this study and in the azo cases of Table V is the extent of randomization of positions of the radicals in the cage prior to termination. The closest measure of this by experiments of the type presented here and in the azo studies would appear to be the rate of "turnover" of 1-phenylethyl radical (k_{rot}) relative to the rate of the termination reactions in the cage ($k_{\text{comb}} + k_{\text{disp}}$). The rates of these termination reactions are a function of the diffusive displacement of the CO_2 from between the two caged

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[20] Note that k_{comb} and k_{disp} are not the usual second-order termination constants but are first-order rate constants for the conversion of the radical pair cages of Scheme I to the combination and disproportionation products.

[21] Errors in the cage effect are not thought to be large; however, determination of the cage effect, F, involves two extrapolations (see Results section).

[22] The equations of Kopecky (ref 9) could have been applied directly to obtain the relative k's; a modified treatment is used here to emphasize the simple relationship shown in eq 8.

TABLE V

RELATIVE RATES (HORIZONTAL COMPARISON)

Compd	k_{comb}	k_{disp}	k_{rot}	k_{diff}	$\frac{k_{rot}{}^a}{k_{cage\ reaction}}$	Retention of configuration, %
S-(+)-1[b]	1	3.2	19	5.8	4.5	21
Azobis-1-phenylethane[c]	1	0.14	15	2.4	12	20.5
S-(−)-1,1′-Diphenyl-1-methylazomethane[d]	1	0.1	10–17	2–3	~12	10–17
Azobis-2-phenyl-3-methylbutane[e]	1		Very small			>95
3,6-Dimethyl-3,6-diethyl-1,2-pyridazine[f]	1		0.02			98

[a] $k_{cage\ reaction} \equiv k_{combination} + k_{disproportionation}$. [b] This work, 60° in cumene, cage effect 0.47. [c] Reference 8, 105° in benzene, cage effect 0.32. [d] Reference 9, 100° in several solvents, cage effect ~0.3. [e] P. D. Bartlett and J. M. McBride, *Pure Appl. Chem.*, **15**, 89 (1967); photolysis in frozen benzene (−196°). [f] Reference 7.

radicals, plus any further energy requirements in the interactions of these two radicals. The principal conclusion from this study, and from the acyclic azo cases of Table V (second and third entries), is that considerable randomination of the positions of the radicals occurs in the cage prior to termination. The value of k_{rot}/k_{cage} reaction for the perester case is approximately 4.5; the corresponding values for the azo cases are approximately 12.

Differences in the radicals involved, in the intervening molecule (CO_2 *vs.* N_2), in solvent, and in temperature render further comparisons at this point of limited value. One might comment, however, on the apparent similarity in the ratio of k_{rot}/k_{comb} for the perester and the azo cases in contrast to the difference in the ratio of $k_{rot}/(k_{comb} + k_{disp})$ indicated above. The higher value of k_{rot}/k_{comb} for the perester is a consequence of the large amount of disproportionation in the cage. The major barrier to the cage reactions in this case may be associated with diffusion of the carbon dioxide from between the two radicals. This carries the implication that the *sum* of k_{comb} plus k_{disp} would be constant here; *i.e.*, had disproportionation been less important, combination would have been more important. Under these circumstances the degree of retention of configuration in the cage ether and the ratio of k_{rot}/k_{cage} reaction could be the same as reported in Table V, even though the ratio of k_{rot}/k_{comb} were smaller.

Experimental Section

2-Phenylpropionic acid was prepared by the method of Eliel and Freeman,[23] bp 145–150° (10 mm), $n^{25}D$ 1.5218 [lit.[23] bp 144–147° (11 mm), $n^{25}D$ 1.5213].

S-(+)-**2-Phenylpropionic Acid.**—2-Phenylpropionic acid was resolved with strychnine according to the procedure of Arcus and Kenyon[24] with the modification that the salt was dissolved in an excess of 75% ethanol–water and then the excess solvent was removed under vacuum. This method was superior to heating the solvent to dissolve the salt, because heating led to slow decomposition of the salt.

2-Phenylpropanoyl chloride was prepared from 2-phenylpropionic acid and thionyl chloride (by the method of Greene),[25] bp 50° (0.15 mm) [lit.[25] bp 93–94° (11 mm)].

S-(+)-*tert*-**Butyl 2-phenylperpropionate** was prepared by a modification of a literature procedure.[13a] *S*-(+)-2-Phenylpropanoyl chloride (17.0 g) in an equal volume of ether was added very slowly to a solution of *tert*-butyl hydroperoxide (22 ml) in 20 ml of pyridine and 15 ml of ether cooled in an ice–acetone bath. The reaction was stirred for 4 hr at 0°. Saturated aqueous sodium chloride was added to the reaction mixture and the aqueous layer was extracted three times with ether. The ethereal layer was washed with three portions of 10% aqueous sulfuric acid and with saturated aqueous sodium bicarbonate and dried ($MgSO_4$). The ether was removed under reduced pressure. The remaining *tert*-butyl hydroperoxide was partially removed by trap-to-trap distillation.

A 1.429-g sample of perester ($[\alpha]^{25}D$ +23.44°) was dissolved in 50 ml of ether and washed with 100 ml of cold 5% aqueous KOH. The ether solution was dried ($MgSO_4$) and the ether was removed at room temperature. Nmr analysis of the perester showed less than 1% *tert*-butyl hydroperoxide and $[\alpha]^{25}D$ +24.98°. Thus the washing with cold 5% aqueous potassium hydroxide did not racemize the perester. The remainder of the perester was dissolved in 300 ml of ether, washed with three 300-ml portions of cold 5% aqueous KOH and once with saturated aqueous NaCl, and dried ($MgSO_4$). The ether was removed under vacuum at room temperature and the nmr analysis of the perester showed only trace amounts of *tert*-butyl hydroperoxide.

The *S*-(+)-*tert*-butyl 2-phenylperpropionate could be recrystallized at low temperature from pentane. Approximately 2 g of perester was dissolved in 10 ml of pentane in a centrifuge tube and cooled to −78°. The first crystallization gave a very fine precipitate which after three or four more recrystallizations gave long needles which melted below room temperature. Racemic mixtures of *tert*-butyl 2-phenylperpropionate were much more difficult to recrystallize and did not give a nicely crystalline product. The data for the pure *tert*-butyl 2-phenylperpropionate were $n^{25}D$ 1.4868, $[\alpha]^{25}D$ 25.5° (*c* 11.60 in $CHCl_3$). The optical purity of the starting *S*-(+)-2-phenylpropionic acid was 96.8%; therefore the rotation for optically pure perester is $[\alpha]^{25}D$ 26.3°: ir (CCl_4) 3060 (w), 3025 (w), 2980 (s), 2930 (m), 1770 (s), 1600 (w), 1485 (w), 1390 (w), 1370 (m), 1190 (m), 1120 (m), 1080 (m), 1050 (m), 850 (m), 750 (m), 720 (w), and 695 cm^{-1} (m); nmr (CCl_4) 1.12 (9 H, s), 1.45 (3 H, d, $J = 7$ Hz), 3.65 (1 H, q, $J = 7$ Hz), 7.25 (5 H, s); $[\alpha]^{25}_{578}$ 27.8, $[\alpha]^{25}_{546}$ 32.6, $[\alpha]^{25}_{436}$ 66.0, $[\alpha]^{52}_{365}$ 121.8°.

S-(−)-1-**Phenylethanol.**—1-Phenylethyl hydrogen phthalate was prepared by the method of Houssa and Kenyon,[26] mp 106–108° (lit.[26] mp 107–108°). Brucine (52 g, 0.132 mol) was dissolved in a warm solution of racemic 1-phenylethyl hydrogen phthalate (35.6 g, 0.137 mol) in 200 ml of acetone. The solution was placed in the freezer (−27°) and allowed to crystallize overnight. The supernatant liquid was decanted from the crystals and the crystals were redissolved in methyl acetate. Heating the methyl acetate solution to speed solution of the salt led to a gradual decomposition of the salt; thus the salt was dissolved by vigorously stirring the suspension at room temperature and then placing the solution in the freezer. After three recrystallizations the salt was decomposed with 10% hydrochloric acid. The phthalate obtained was hydrolyzed in 5 *N* sodium hydroxide on a steam bath for 1 hr. The reaction mixture was extracted with ether and the ethereal layer was washed with saturated aqueous NaCl and dried ($MgSO_4$). The ether was removed and the alcohol was distilled, bp 70° (2.5 mm), to

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give 5 g of alcohol, $[\alpha]^{20}_{436}$ −8.165° (9.00% optically pure), n^{25}_{D} 1.5251 (lit.[22] n^{25}_{D} 1.5267).

S-(−)-*tert*-Butyl 1-Phenylethyl Ether. Method A.—Powdered silver nitrate (3.74 g, 0.212 mol) was added in small amounts to a solution of *S*-(−)-1-phenylethanol (1.29 g, 0.0106 mol, 9.00% optically active) and *tert*-butyl chloride (1.96 g, 0.0202 mol) in 2.14 g of triethylamine cooled to 0°. After the addition was complete, the reaction mixture was filtered and diluted with ether. The ether layer was washed with 10% aqueous HCl and saturated aqueous sodium bicarbonate and dried ($MgSO_4$). The solvent was removed and the product was chromatographed on alumina (I) using ether–hexane (1:9) as the eluent. The product was found in the first three fractions (approximately 150 ml). The solvent was removed and the product was collected by vpc (SE-30 at 100°) to give 0.100 g (5%): $[\alpha]^{25}_{436}$ −19.6° (*c* 5.01, ethanol) which corresponds to a rotation of $[\alpha]^{25}_{436}$ −218° for the optically pure *S*-(−)-1-phenylethyl *tert*-butyl ether; nmr (CCl_4) δ 1.13 (9 H, s), 1.31 (3 H, d, $J = 7$ Hz), 4.62 (1 H, q, $J = 7$ Hz), 7.35 (5 H, broad s). *Anal.* Calcd: C, 80.85; H 10.18. Found: C, 80.74; H, 10.27.

Method B.—A mixture of *S*-(−)-1-phenylethanol (1.6287 g, 13.3 mmol, 9.06% optically active), 2.46 g (26.6 mmol) of *tert*-butyl chloride, and 3.22 g (26.6 mmol) of 2,4,6-trimethylpyridine was degassed and sealed in Pyrex tubes. The tubes were then placed in a steam cone (110°) for 4 days. The tubes were opened and the reaction mixture was separated by vpc (SE-30, 100°) to give 0.213 g (9% yield) of *S*-(−)-*tert*-butyl 1-phenylethyl ether, $[\alpha]^{25}_{436}$ −19.05° (*c* 10.65 ethanol). The polarimeter sample was then recollected from vpc (SE-30, 100°) to give a sample with a rotation of $[\alpha]^{25}_{436}$ −19.36° which corresponds to a rotation of $[\alpha]^{25}_{436}$ −214° for optically pure ether. The rotations from method A and B were averaged to give $[\alpha]^{25}_{436}$ −216°.

Cage Yield of *tert*-Butyl 1-Phenylethyl Ether.—Pyrex test tubes with solutions of perester and butanethiol in cumene or benzene as solvent were degassed, sealed, and placed in a constant-temperature bath at 60° for 45 hr (30 half-lives). The tubes were opened and 1,2-dichlorobenzene was added as an internal standard for vpc analysis. The results are summarized in Table IV.

Decomposition of *S*-(+)-*tert*-Butyl 2-Phenylperpropionate in Cumene.—A 5.0-ml aliquot of perester in cumene (0.11 *M*) and 5.0 ml of butanethiol solution in cumene (1.0 *M*) were placed in each of ten tubes. The tubes were degassed (three freeze–thaw cycles), sealed, and placed in a constant-temperature bath at 60° for 24 hr (16 half-lives). The tubes were opened and trap-to-trap distilled; teflon spinning band distillation removed some of the solvent. The residual solution was then passed through the gc (SE-30 at 100°) and collected, followed by gc on Carbowax 20M from which the products were collected and identified by comparison with authentic samples.

Decomposition of *tert*-Butyl 2-Phenylperpropionate in Cumene in the Presence of Excess Koelsch's Radical.—A decomposition mixture 1.85×10^{-3} *M* in Koelsch's radical[17c] and 0.93×10^{-3} *M* in perester was placed in a Pyrex uv cell; the mixture was degassed and sealed. The decomposition was carried out at 60° and followed at 860 nm using a Beckman DU-I. The rate of disappearance of Koelsch's radical was not first order, indicated greater than 100% efficiency, and gave scavenged products which were not stable to the reaction conditions.

Decomposition of *tert*-Butyl 2-Phenylperpropionate in the Presence of 1–2% Koelsch's Radical.[17c]—A decomposition mixture 0.0147 *M* in perester and 3.4×10^{-4} *M* in Koelsch's radical (2.3%) was degassed and sealed in a Pyrex uv cell. The sample was given a preliminary warm-up at 41.6° for 2 min and then placed in the sample cavity of the DU-I, which was thermostated at 40.7°. The decomposition was followed to the complete disappearance of the Koelsch's radical. The disappearance of Koelsch's radical was zero order. The decomposition at 30.1 and 48.3° was executed in the same manner as the above.

Kinetics of the Perester Decomposition.—A solution of perester (0.0652 g/10 ml of cumene, 0.0239 *M*) was placed in seven sample tubes and decomposed at 60.10°. The tubes were removed from the bath and quenched at 0°. The tubes were then stored in the freezer (−27°) until the completion of the run, at which time all the samples were analyzed by ir at the carbonyl absorption ($\nu_{\max}$ 1770 cm^{-1}, ϵ 56 M^{-1} mm^{-1}, $b = 0.50$ mm). The decomposition at 80.50° was carried out in exactly the same manner as that given above. In the decompositions at 40°, the samples were analyzed when the tube was removed from the bath because long storage of the decomposition samples led to erratic results. The infrared spectrophotometer was a Perkin-Elmer 237B; a normal slit width and slow scan speed were used. Due to the difficulty in maintaining the pen at the $\nu_{\max}$, the 1765–1790 cm^{-1} region of the spectrum was scanned twice for each sample and the absorbances were averaged. The plots of the logarithm of the perester concentration *vs.* time were linear for at least two to three half-lives. Infinity points taken after ten half-lives showed no detectable carbonyl absorption. The results are summarized in Table III.

Hydrolysis of *R*-(−)-2-Phenylpropanoyl Chloride.—*R*-(−)-2-Phenylpropanoyl chloride prepared from *R*-(−)-2-phenylpropionic acid, $[\alpha]^{25}_{\mathrm{D}}$ −48.5° ($CHCl_3$), was hydrolyzed with 20% aqueous KOH at 0°. The reaction mixture was extracted with ether and the aqueous layer was acidified with 10% aqueous HCl. The acid was then extracted into ether; the ether layer was washed with saturated aqueous NaCl and dried ($MgSO_4$). The ether was removed under vacuum and the acid was distilled (short path) to give *R*-(−)-2-phenylpropionic acid, n^{25}_{D} 1.5213, $[\alpha]^{25}_{\mathrm{D}}$ −49.9°.

Reduction of *R*-(−)-*tert*-Butyl 2-Phenylperpropionate.—*R*-(−)-*tert*-Butyl 2-phenylperpropionate prepared from *R*-(−)-2-phenylpropanoyl chloride (from 53.8% optically pure acid) was treated with potassium iodide, 2-propanol, acetic acid, and acetic anhydride at room temperature for 2 days. The iodine produced was consumed with aqueous sodium thiosulfate and the acids were extracted into ether. The acids were then extracted into saturated aqueous sodium bicarbonate which was washed with ether and then neutralized with 10% aqueous HCl. The acidified aqueous solution was then extracted with ether. The ether layer was dried ($MgSO_4$) and the ether and some of the acetic acid were removed under vacuum. After two short-path distillations the rotation of the *R*-(−)-2-phenylpropionic acid showed 98% retention of the initial optical activity.

Registry No.—**1**, 3377-90-0; *S*-(+)-**1**, 33122-25-7; *S*-(−)-1-phenylethanol, 1445-91-6; *S*-(−)-*tert*-butyl-1-phenylethyl ether, 33069-10-2; *R*-(−)-2-phenylpropionic acid, 7782-26-5.