Thermal decomposition of optically active unsymmetrical azoalkanes. (−)-(*S*)-1,1′-Diphenyl-1-methylazomethane[1]

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The ratio, $(k_c/k_r)_{\text{cage}}$, of the rate of coupling of the 1-phenylethyl radical with the benzyl radical to the rate of its rotation with respect to the benzyl radical in the solvent cage has been determined for several solvents. The optically pure title compound, (−)-(*S*)-**4**, has been prepared and its absolute configuration determined. Thermal decomposition of (−)-(*S*)-**4** yields (−)-(*R*)-1,2-diphenylpropane, (−)-(*R*)-**9**, with partial retention of configuration. The maximum rotation of (−)-(*R*)-**9** has been determined. At 100° in benzene, cyclohexane, chlorobenzene, (all containing ca. 1 *M* butanethiol) and butanethiol, the cage effects for the decomposition of (±)-**4** were found to be 28.3, 31.7, 33.4, and 18.2%, respectively. Under these conditions (−)-(*R*)-**9** was formed from (−)-(*S*)-**4** with 10.3, 10.9, 13.0, and 17.3% net retention of configuration, respectively. A simple expression for $(k_c/k_r)_{\text{cage}}$ can be derived:

$$(k_c/k_r)_{\text{cage}} = F(1-f)[(-)\text{-}(R)\text{-}\mathbf{9}/(+)\text{-}(S)\text{-}\mathbf{9} - 1]$$

F is the fraction of radicals consumed within the solvent cage and *f* is the fraction of radicals consumed within the solvent cage that disproportionate. Under the above conditions values for $(k_c/k_r)_{\text{cage}}$ were found to be 0.059, 0.069, 0.090, and 0.070, respectively. The values of the cage effect and $(k_c/k_r)_{\text{cage}}$ given were calculated assuming $f = 0.1$, but change little if *f* is assumed to be 0. The relevance of these results to the stereochemistry of the Wittig and Meisenheimer rearrangements and of the decomposition of diacyl peroxides is discussed.

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The stereochemical fate of free radicals generated from optically active precursors has not yet received the systematic study accorded that of carbonium ions and carbanions derived from such sources. This appears to be due to a number of factors including the observations of essentially complete loss of either optical activity (1) or isomeric identity (2) in early systems studied, and ambiguity (3) concerning the mechanisms of decomposition of diacyl peroxides from which optically active products have been obtained (4).

In reactions which almost certainly proceed by radical pathways, stereoselectivity has been observed in the decomposition of substituted pyrazolines (5) and substituted tetrahydropyridazines (6) to substituted cyclopropanes and substituted cyclobutanes, respectively, photochemical decomposition of acyclic azoalkanes in frozen solution at low temperature (7), in a cage disproportionation reaction (8), in perester decompositions under very high pressures of oxygen (9), in addition of hydrogen bromide to olefins at low temperature and at high hydrogen bromide concentration (10), in certain photobromination reactions at low temperature (11), and in the cyclization of a propargylic ester to a γ-lactone (12). In the reactions involving open-chain systems stereoselectivity decreased with both increasing temperature (7, 9–11) and with decreasing concentration of radical trapping species (9–11). In all these cases radicals were generated with either another radical or a very efficient radical trapping species either within or as part of the solvent cage. Only in frozen solution was complete stereospecificity observed (7). It is clear that free radicals formed in the liquid or vapor phase by homolytic fission of a bond at an asymmetric carbon atom cannot maintain asymmetry for longer than ca. 10^{-9} s, if at all. One cannot tell if loss of asymmetry is due to a requirement that the radical assume a planar conformation or is due to rapid interconversion between two pyramidal conformations. Spectral studies of free radicals indicate that the planar conformation is the more stable (13), but radicals can be formed at the bridgehead carbon atom of small, bicyclic ring systems with energy requirements not much greater than in those systems in which radicals can assume a planar conformation (14, 3).

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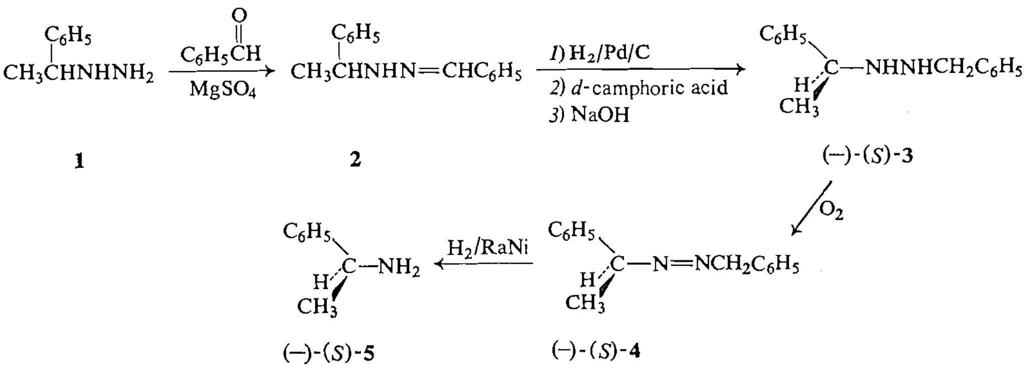
Vinyl radicals also lose geometrical identity quite rapidly (15) and these species can be trapped before isomerization only at low temperatures and with high concentrations of reactive hydrogen atom donors (16).

In order to be able to detect asymmetric products from radical reactions in solution involving asymmetric substrates it is necessary to use a reaction in which radicals are consumed at a rate which can compete with the rates of their diffusion and rotation.

The decomposition of a series of optically active unsymmetrical azoalkanes, eq. [1], appears well suited for a general and systematic investigation of the stereochemical capabilities of free radicals and of the relative rates of the various processes which radicals formed in pairs in close proximity to each other can undergo. The radical nature of the decomposition of azoalkanes is well known and there is good evidence in both cyclic (5*b*, 17) and acyclic (18) systems that the decomposition is a concerted process which gives directly a molecule of nitrogen and a pair of radicals. These can combine at a rate which competes with the rate of their diffusion apart (19). The study of the decomposition of unsymmetrical azoalkanes offers several advantages over that of symmetrical azoalkanes. Separation of diastereomeric starting materials is unnecessary. Stereoselectivity would only be observed as a result of a cage recombination (19) reaction which can produce only the unsymmetrical coupling product R—R′. This product should be easily separable from the symmetrical products, R—R and R′—R′, which are only formed by combination of radicals which have diffused away from their original partners. The yield of symmetrical coupling products is dependent upon the proportion of radicals which diffuse away from their original partners. This could allow an estimate to be made of the proportion of cage recombination which occurs without recourse to the radical counting techniques usually required, and/or allow an estimate to be made of the relative rates of coupling between various radicals. Finally, the nature of the groups R and R′ can be varied independently and in a way that the stereochemistry of even bulky radicals can be studied. For example, if R is big, R′ can be made small so that a significant amount of cage recombination might still occur. Only a very small amount of cage recombination is observed in decomposition in solution of symmetrical azoalkanes with bulky alkyl groups (7).

$$[1] \quad \text{R—N=N—R}' \rightarrow \text{R—R}' + \text{R—R} + \text{R}'\text{—R}' + \text{N}_2$$

The preparation and some studies of the decomposition of racemic and optically active 1,1′-diphenyl-1-methylazomethane are presented in this report. After the experimental work reported in this paper had been completed a report of the stereochemistry of decomposition of (−)-1,1′-diphenylazoethane was presented (20). The results described in that report are in excellent agreement with those of the present study.



$[\alpha]_D^{25}$ −31.4°(*c*, 5.4, dioxane) $[\alpha]_D^{25}$ −125° (*c*, 1.06, benzene)

Rotations given are experimentally observed

CHART I

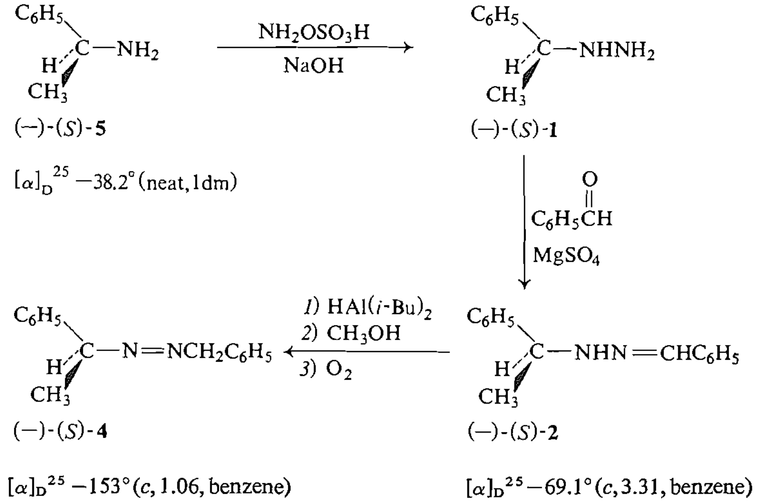
Absolute Configurations of Starting Material and Product

The preparation of (−)-(*S*)-1,1′-diphenyl-1-methylazomethane, (−)-(*S*)-**4**, and its degradation to (−)-(*S*)-1-phenylethylamine, (−)-(*S*)-**5**, are outlined in Chart I.

N-Benzyl-*N*′-(1-phenylethyl)-hydrazine, **3**, was prepared by condensation of 1-phenylethylhydrazine, **1** (18*c*), with benzaldehyde followed by reduction of the benzaldehyde 1-phenylethylhydrazone, **2**, formed. The compound, **3**, was quite sensitive to air oxidation and was readily oxidized to **4** by stirring solutions containing it under an atmosphere of oxygen. The azoalkane, **4**, was very sensitive to acid, base, and light. Rearrangement to the hydrazone, **2**, occurred readily under the influence of any one of these catalysts. This behavior contrasts with that of 1,1′-diphenylazoethane which in our hands is much less sensitive. Distillation of **4** was not attempted. It was purified by concentration of solutions containing it until the refractive index of the residual oil remained constant. When the preparation of **4** was carried out in the dark using carefully neutralized apparatus, the product was analytically pure, contained less than 1–2% hydrazone, **2**, as determined by ultraviolet (u.v.) spectroscopy, and no extraneous peaks could be detected in its nuclear magnetic resonance (n.m.r.) spectrum.

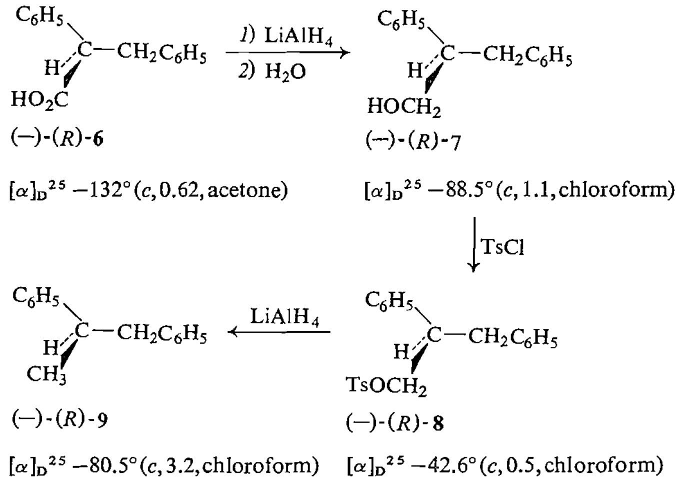
The resolution of **3** was accomplished by fractional crystallization of the *d*-camphorate salt until the rotation of the salt remained constant. Attempts to obtain the rotation of (−)-(*S*)-**3** gave variable results because of its ready oxidation to (−)-(*S*)-**4**. A sample of (−)-(*S*)-**4**, $[\alpha]_D^{25}$ −152° (*c*, 1.06, benzene), was hydrogenolyzed with Raney nickel in methanol at 25° to (−)-(*S*)-1-phenylethylamine, (−)-(*S*)-**5**, $[\alpha]_D^{25}$ −31.4° (*c*, 5.4, dioxane), whose absolute configuration is established (21) and whose maximum rotation (22) under these conditions was determined: $[\alpha]_D^{25}$ −39.6° (*c*, 5.4, dioxane). This result indicates that either this sample of (−)-(*S*)-**4** was 79% optically pure or racemization took place under the conditions of the hydrogenolysis. There was no racemization of (−)-(*S*)-**5** under the reaction conditions. Racemization could occur before hydrogenolysis, either by the process involved in the racemization which accompanies reduction in the catalytic hydrogenation of (−)-(*R*)-3-phenyl-1-butene to (−)-(*R*)-2-phenylbutane (23), or as a result of isomerization, by base adsorbed on the catalyst, of (−)-(*S*)-**4** to the benzylhydrazone of acetophenone, **10**, followed by reduction and hydrogenolysis.

In an alternate attempt to determine the maximum rotation of (−)-(*S*)-**4** a sample (−)-(*S*)-**5**, $[\alpha]_D^{25}$ −36.6° (neat, *l* 1 dm), was converted to



Rotations given are for optically pure compounds

CHART II



Rotations given are for optically pure compounds; Ts = *p*-toluenesulfonyl

CHART III

(−)-(*S*)-**4**, $[\alpha]_D^{25}$ −146° (*c*, 1.36, benzene),[3] by a route which quite certainly does not affect the asymmetric center (Chart II). On the basis that the maximum rotation of (−)-(*S*)-**5** is 38.2° (neat, *l* 1 dm) (22) the maximum rotation of (−)-(*S*)-**4** determined in this manner would then be −153°. This is essentially identical with the value obtained by resolution, and (−)-(*S*)-**4** of $[\alpha]_D^{25}$ −152° must be optically pure or very nearly so.

The absolute configurations of the 1,2-diphenylpropanes, (+)- and (−)-**9**, the unsymmetrical coupling products expected from decomposition of (+)-(*R*)- and (−)-(*S*)-**4**, have been determined (24), but there appeared to be some doubt about the maximum rotation of these compounds. Values of $[\alpha]_D^{19}$ −63.5° (24), $[\alpha]_D^{25}$ +76.7° (25), and $[\alpha]_D^{25}$ −76.3° (25) (all *c*, 2.2–2.3, chloroform) have been reported for these materials prepared by different routes. An independent determination of the maximum rotation of these materials seemed necessary[4] and was carried out by the route shown in Chart III. Optically pure (−)-(*R*)-2,3-diphenylpropanoic acid, (−)-(*R*)-**6** (28), was converted to (−)-(*R*)-**9**, $[\alpha]_D^{25}$ −80.5° (*c*, 3.2, chloroform), by reactions which did not involve the asymmetric center. This sequence establishes chemically the absolute configuration of (−)-(*R*)-**6**[5] as well as the maximum rotations of (−)-(*R*)-**9** and the intermediates shown in Chart III. The enantiomers of **9** prepared previously were clearly not optically pure (25).

Kinetic Studies

The rates of decomposition of **4** in cumene were determined by measuring the rates of nitrogen evolution. An insufficient amount of nitrogen was evolved in each of the kinetic runs and plots of log $(V_\infty - V_0)/(V_\infty - V_t)$ vs. time showed considerable curvature, especially at the lower temperature. The rate constants given in Table I were determined from the initial slopes of the plots using the theoretical values for V_∞. The initial rates are independent of concentration. An n.m.r. spectral analysis of a run at 106° indicated that considerable amounts of hydrazone, **2**, had been formed. There was no evidence for the presence of any of the isomeric hydrazone, acetophenone benzylhydrazone, **10**. It was

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[3] After correction for the presence of 8 mole % of (−)-(*S*)-**1**.

[4] Raney nickel reduction of a sample of (−)-(1*S*,2*S*)-1,2-diphenyl-1-propanol (26) afforded the enantiomer with $[\alpha]_D^{25}$ − 76.3°, while the enantiomer with $[\alpha]_D^{25}$ +76.7° had been prepared by a sequence involving Raney nickel hydrogenolysis of a hydroxyl group at the asymmetric center. This hydrogenolysis would have to have proceeded with 100% retention of configuration if the (−)-enantiomer were optically pure and if no optical fractionation occurred during further reactions leading to the (+)-enantiomer. Such a high degree of stereospecificity does not appear to occur in Raney nickel hydrogenolyses of other systems (27).

[5] The absolute configuration of (+)-(*S*)-**6** has been assigned correctly on the basis of empirical methods (29). Also, (+)-methyl-1,2-methyl-1,2-diphenylpropionate, obtained by a degradation process, has been converted to (+)-(*S*)-**9** (25).

TABLE I

Rates of decomposition of **4** in cumene

Temperature (°C)	Concentration (M)	Moles N_2†	k‡ $\times 10^6$ (s^{-1})
106.0	0.084	0.59	8.44
	0.15	0.69	8.05
	0.13	0.67	8.29
127.9	0.12	0.90	124
	0.18	0.83	120
	0.15	0.86	111

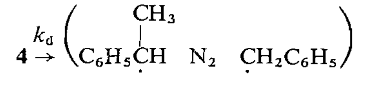
†Moles N_2 per mole of **4**.
‡At 106° ΔH^* 35.6 ± 1.0 kcal/mole, ΔS^* 12.1 ± 2.6 e.u.

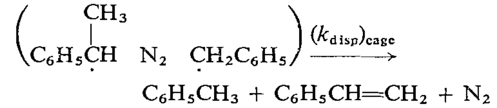
shown in separate experiments that **2** did not evolve nitrogen under these reaction conditions.

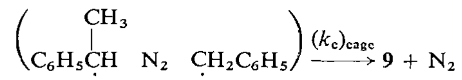
It can be predicted from the summary (30) of the activation parameters of a series of azoalkanes that ΔH^* for the decomposition of **4** should be about 33.5–34.5 kcal/mole and ΔS^* about 6 e.u. The value of ΔH^* obtained for the decomposition of **4**, Table I, is in good agreement with this prediction but the value for ΔS^* appears to be significantly different.

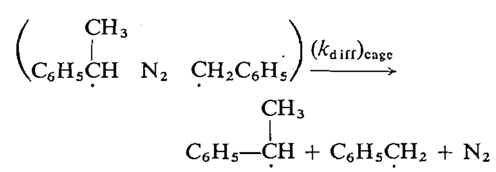
Products

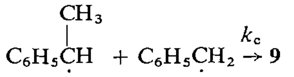
Decomposition of **4** in benzene solution results in the formation of products according to eqs. [5]–[13]. The decomposition of **4** produces benzyl radicals and 1-phenylethyl radicals in a solvent cage (19). These radicals can react within the solvent cage to form the unsymmetrical coupling product, **9**, and the disproportionation products styrene and toluene, or in a competitive process, diffuse away from each other. The radicals which have diffused away from the solvent cage may now encounter and react with one of their own kind. An encounter between two 1-phenylethyl radicals will result in coupling to form *meso* and *dl*-2,3-diphenylbutane, *meso*- and *dl*-**11**, and in disproportionation to form styrene and ethylbenzene. The only reaction resulting from an encounter between two benzyl radicals will be coupling to form bibenzyl. An encounter between a 1-phenylethyl radical and a benzyl radical will result in the same products as are formed in the original solvent cage. The product distributions over a range of concentrations are given in Table II. No styrene could be found in the run at 0.5 M **4**. It was probably consumed by radical addition reactions. The amounts of the low molecular weight products, styrene, ethylbenzene, and toluene, formed in runs at the lower concentrations in benzene, could not be determined because the benzene peak in the gas–liquid chromatogram (g.l.c.) was so broad.

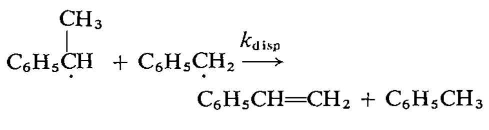
[5]

$$4 \xrightarrow{k_d} \left(\mathrm{C_6H_5}\overset{\mathrm{CH_3}}{\overset{|}{\dot{\mathrm{C}}\mathrm{H}}}\quad \mathrm{N_2}\quad \dot{\mathrm{C}}\mathrm{H_2C_6H_5}\right)$$

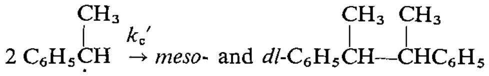
[6]

$$\left(\mathrm{C_6H_5}\overset{\mathrm{CH_3}}{\overset{|}{\dot{\mathrm{C}}\mathrm{H}}}\quad \mathrm{N_2}\quad \dot{\mathrm{C}}\mathrm{H_2C_6H_5}\right) \xrightarrow{(k_{\mathrm{disp}})_{\mathrm{cage}}} \mathrm{C_6H_5CH_3 + C_6H_5CH{=}CH_2 + N_2}$$

[7]

$$\left(\mathrm{C_6H_5}\overset{\mathrm{CH_3}}{\overset{|}{\dot{\mathrm{C}}\mathrm{H}}}\quad \mathrm{N_2}\quad \dot{\mathrm{C}}\mathrm{H_2C_6H_5}\right) \xrightarrow{(k_{\mathrm{c}})_{\mathrm{cage}}} \mathbf{9} + \mathrm{N_2}$$

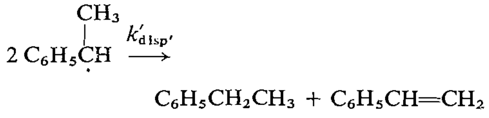
[8]

$$\left(\mathrm{C_6H_5}\overset{\mathrm{CH_3}}{\overset{|}{\dot{\mathrm{C}}\mathrm{H}}}\quad \mathrm{N_2}\quad \dot{\mathrm{C}}\mathrm{H_2C_6H_5}\right) \xrightarrow{(k_{\mathrm{diff}})_{\mathrm{cage}}} \mathrm{C_6H_5{-}}\overset{\mathrm{CH_3}}{\overset{|}{\dot{\mathrm{C}}\mathrm{H}}} + \mathrm{C_6H_5}\dot{\mathrm{C}}\mathrm{H_2} + \mathrm{N_2}$$

[9]

$$\mathrm{C_6H_5}\overset{\mathrm{CH_3}}{\overset{|}{\dot{\mathrm{C}}\mathrm{H}}} + \mathrm{C_6H_5}\dot{\mathrm{C}}\mathrm{H_2} \xrightarrow{k_c} \mathbf{9}$$

[10]

$$\mathrm{C_6H_5}\overset{\mathrm{CH_3}}{\overset{|}{\dot{\mathrm{C}}\mathrm{H}}} + \mathrm{C_6H_5}\dot{\mathrm{C}}\mathrm{H_2} \xrightarrow{k_{\mathrm{disp}}} \mathrm{C_6H_5CH{=}CH_2 + C_6H_5CH_3}$$

[11]

$$2\,\mathrm{C_6H_5}\overset{\mathrm{CH_3}}{\overset{|}{\dot{\mathrm{C}}\mathrm{H}}} \xrightarrow{k_c'} \textit{meso-}\text{ and }\textit{dl-}\mathrm{C_6H_5}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}\mathrm{H}}}{-}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}\mathrm{H}}}\mathrm{C_6H_5}$$

meso- and *dl*-**11**

[12]

$$2\,\mathrm{C_6H_5}\overset{\mathrm{CH_3}}{\overset{|}{\dot{\mathrm{C}}\mathrm{H}}} \xrightarrow{k_{\mathrm{disp}}'} \mathrm{C_6H_5CH_2CH_3 + C_6H_5CH{=}CH_2}$$

[13] $$2\,\mathrm{C_6H_5}\dot{\mathrm{C}}\mathrm{H_2} \xrightarrow{k_c''} \mathrm{C_6H_5CH_2CH_2C_6H_5}$$

The ratio of the two kinds of symmetrical coupling products, *meso*- and *dl*-**11** to bibenzyl, decreases as the initial concentration of **4** decreases to a limiting value of about 0.90–0.94. The larger ratio at the higher initial concentrations of **4** reflects the greater reactivity of the benzyl radical as compared to the 1-phenylethyl radical in hydrogen abstraction from **4** and from reaction products, and in addition to any styrene formed. As the initial concentration of **4** is decreased such radical–molecule reactions become less important. The fact that the ratio, *meso*- and *dl*-**11** to bibenzyl, tends to a limit indicates that at an initial concentration of **4** of

TABLE II

Product distribution from thermal decomposition of **4** at 110° in benzene

[4]* (*M*)	Relative yield (%)					Ratio of *meso*- + *dl*-**11**: bibenzyl
	Toluene	Ethyl-benzene	Bibenzyl	**9**	*meso*- + *dl*-**11**†	
0.5	18	12	7.1	44	17.5	2.5
0.03	—	—	12.7, 12.0	65.3, 70.9	22.0, 17.1	1.7, 1.4
0.0063	—	—	16.9, 17.1	63.3, 64.0	19.8, 18.9	1.2, 1.1
0.0013	—	—	17.7, 19.7	65.6, 63.4	16.7, 17.3	0.94, 0.90

*Not corrected for volume expansion.
†Equal amounts of *meso*- and *dl*-**11** were formed.

ca. 1×10^{-3} *M*, all radicals produced are consumed by radical–radical reactions. The ratio would be expected to be 1.0 if there were no disproportionation between two 1-phenylethyl radicals, and if the rate constants for the coupling reactions that form bibenzyl, **9** and *meso*- and *dl*-**11** are all equal (see below). The actual ratio indicates that there is ca. 6–10% disproportionation. This appears to be a reasonable value. The amount of disproportionation observed during the decomposition of azocumene is 6% (30). No attempt was made in this study to determine accurately the amount of disproportionation which occurs during the decomposition of **4** and no study seems to have been made of the disproportionation occurring during decomposition of 1,1′-diphenylazoethane, but there is no reason to believe that disproportionation in these systems will be much different from 6–10%.

Cage Effect

If the radicals derived from **4** which have diffused from the original solvent cage couple randomly, an estimate of the cage effect in the decomposition of **4** may be made on the basis of the relative yields of the coupling products in decompositions at low initial concentrations of **4**. In the absence of disproportionation the amounts of bibenzyl, **9** and the sum of *meso*- and *dl*-**11** formed outside the original solvent cage would be in the ratio 1:2:1. The amount of **9** formed in excess of this ratio would represent the amount of **9** formed by cage recombination. In practice there is disproportionation which reduces the relative amounts of **9**, *meso*- and *dl*-**11** which would otherwise be formed. Noting that in the absence of disproportionation the amounts of *meso*- plus *dl*-**11** should equal the amount of bibenzyl formed, and correcting the amount of **9** found by the amount of disproportionation which occurs between benzyl and 1-phenylethyl radicals, the cage effect can be calculated from eq. [13]. The assumption

$$[13] \quad \%\ \text{cage recombination} = 100\left(\frac{\mathbf{9} - 2 \times \text{bibenzyl}}{\mathbf{9} + 2 \times \text{bibenzyl}}\right)$$

is also made that the amount of disproportionation is the same within the original solvent cage as it is without.

The cage effect can also be calculated from the product distribution resulting from the decomposition of **4** in the presence of butanethiol. Butanethiol will scavenge all radicals which diffuse away from the original solvent cage, converting them to toluene and ethylbenzene. This assumption is shown to be correct for no trace of the symmetrical coupling products, bibenzyl and *meso*- and *dl*-**11** can be found when **4** is decomposed in the presence of butanethiol. The cage effect can then be calculated from the relative yields of **9** and ethylbenzene or toluene. Such a procedure has previously been used in the study of the decomposition of azocumene (31).

There are two values for the size of the cage effect for each entry in Table III. One value is calculated without correction for disproportionation between the benzyl and the 1-phenylethyl radicals. The other is calculated assuming 10% disproportionation. For the runs in the presence of butanethiol there is a difference of from 1.2 to 3% between these values depending on the magnitude of the cage effect and the method by which it is obtained. It is likely that 10% disproportionation is a maximum value so that the true values of the cage effects probably lie between the "corrected" and "uncorrected" values listed in Table III. The size of the cage

TABLE III

Cage effects in the decomposition of **4**

Solvent	[4] (M*)	[C_4H_9SH] (M)*	Temperature (°C)	% Cage reaction†	
				Uncorrected‡	Corrected§
Benzene	0.0013	0	110	30.2, 24, 4	34.4, 28.5
Benzene	0.13	0.97	110	26.3±0.5	28.3±0.5
Cyclohexane	0.09	1.3	115	29.7±0.4	31.7±0.4
Chlorobenzene	0.30	1.1	108	30.4±0.2	33.4±0.2
Butanethiol	0.22	9.3	110	16.9±0.8	18.2±0.8

*Concentrations refer to solutions as made up at 25° and are not corrected for solvent expansion.

†Values from runs in the presence of butanethiol are averages of at least 3 determinations, and are based on relative yields of ethylbenzene and 9 except in chlorobenzene. In chlorobenzene, values are based on relative yields of toluene and 9. Values in first entry are calculated using eq. [13]. Errors are average errors.

‡Calculated from experimentally observed product ratios.

§Calculated from experimentally observed product ratios corrected for an assumed 10% disproportionation between benzyl and 1-phenylethyl radicals.

effect in solvent butanethiol is considerably smaller than it is in the other three solvents. This is probably due to a solvent effect and not due to scavenging of radicals from within the solvent cage or of interception to secondary recombination processes. The rate constant for hydrogen atom abstraction from benzylmercaptan by the benzyl radical is 5.1 × 10^4 M^{-1} s^{-1} at 25° (32). The rate constants for hydrogen atom abstraction from butanethiol by the radicals derived from **4** should have a similar magnitude and are surely much too small for butanethiol to interfere with primary and secondary recombination processes (19) in the present system.

The presence of ca. 1 M butanethiol in the other solvents probably reduces the size of the cage effect by about 2% from what it would be in the pure solvents. The solvent order of increasing size of the cage effect, benzene, cyclohexane, chlorobenzene is also observed in the decomposition of azocumene (31), where the difficulties involved in interpreting such solvent effects have already been discussed. The "corrected" cage effect for the decomposition of **4** in benzene containing butanethiol agrees well with the value of 29% found for the cage effect found in the decomposition of 1,1′-diphenylazoethane at 105° in benzene (18*e*). This is a system for which a cage effect similar to that found in the decomposition of **4** is to be expected (7).

There is considerable error in calculating cage effects from product distributions in the absence of scavenger using eq. [13] in the present system (first entry in Table III). The products upon which this calculation is based are eluted quite closely together under the best g.l.c. conditions we were able to obtain. Small samples had to be injected to prevent overlap so that peak heights probably were not optimum. There is, however, fair agreement between these "corrected" values and the "corrected" value found in benzene in the presence of 0.97 M butanethiol. This indicates that radicals which have escaped from the original solvent cage do in fact react in a random manner. The difference in stability between benzyl and 1-phenylethyl radicals is not reflected in the rates of their various reactions among each other. Lack of sensitivity to radical stability in the rate of radical–radical coupling reactions (33) and the relative rates of coupling and diffusion of radicals formed in a solvent cage (7) have already been noted.

Attempts to determine the cage effect in the photochemical decomposition of **4** were unsuccessful. Photolysis of **4** resulted in the almost exclusive formation of the hydrazones, **2** and **10**. Similar results were obtained in the photolysis of *cis*-3,6-diphenyl-3,4,5,6-tetrahydropyridazine (6*b*), in which mainly the corresponding hydrazone was formed.

Stereochemistry of Cage Recombination

Optically pure (−)-(*S*)-**4** was decomposed thermally in several solvents with and without butanethiol as scavenger. In all cases the unsymmetrical coupling product, (−)-(*R*)-**9**, was formed. It was shown above that (−)-(*S*)-**4** and (−)-(*R*)-**9** have the same configuration so that (−)-(*R*)-**9** is formed with retention of configuration. The results in Table IV show that extensive racemization has occurred even in the presence of butanethiol where the unsymmetrical coupling

TABLE IV

Stereochemistry of (−)-(*R*)-**9** from the thermal decomposition of (−)-(*S*)-**4**, $[\alpha]_D^{25}$ −152°

Solvent	Temperature (°C)	[4]* (*M*)	$[C_4H_9SH]$* (*M*)	$[\alpha]_D^{25}$ (deg)†	Retention (%)	$(k_c/k_r)_{cage}$‡	
Benzene	132	0.13	0	−3.28	4.1		
	132	0.12	1.7	−9.29	11.5		
	110	0.082	0	−4.49	5.6		
	110	0.13	1.2	−8.27	10.3	0.059	0.061
	110	0.13	4.8	−13.5	16.7		
Butanethiol	110	0.19	9.3	−13.9	17.3	0.069	0.071
	132	0.14	9.3	−11.7	14.5		
Chlorobenzene	107	0.27	0	−6.60	8.2		
	107	0.33	1.1	−11.5	13.0	0.090	0.091
Cyclohexane	115	0.089	0	−5.10	6.3		
	115	0.089	1.3	−8.8	10.9	0.070	0.071
			0				

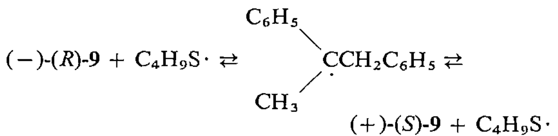
*Not corrected for volume expansion.

†Rotation of (−)-(*R*)-9 taken in chloroform, *c* 1–2. Optically pure (−)-(*R*)-9 has $[\alpha]_D^{25}$ −80.5° (*c*, 3.2, chloroform).

‡Values in first column calculated on basis of "corrected" cage effect, Table III; values in second column calculated on basis of "uncorrected" cage effect, Table III.

product is formed only by recombination within the original solvent cage. It is possible that the low optical yield obtained in the presence of butanethiol is due to racemization of starting material and product as a result of reversible hydrogen atom abstraction from these materials by butanethiyl radicals as shown in Chart IV. Hydrogen atom abstraction from hydrocarbons

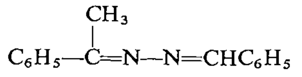
$$C_6H_5\dot{C}HCH_3 \text{ or } C_6H_5\dot{C}H_2 + C_4H_9SH \rightarrow C_6H_5CH_2CH_3 \text{ or } C_6H_5CH_3 + C_9H_9S\cdot$$



$$(-)\text{-}(R)\text{-}\mathbf{9} + C_4H_9S\cdot \rightleftarrows (C_6H_5)(CH_3)\dot{C}CH_2C_6H_5 \rightleftarrows (+)\text{-}(S)\text{-}\mathbf{9} + C_4H_9S\cdot$$

Chart IV

by thiyl radicals is a well known reaction (34). Qualitative evidence that such a hydrogen atom abstraction occurs in the present system is furnished by the observation that small amounts of a light-yellow, low-melting solid were formed in all reactions carried out in the presence of butanethiol. Larger amounts were formed when butanethiol was used as solvent. This material had a g.l.c. retention time similar to that of (−)-(*R*)-**9**. It was not investigated further but is assumed to be the unsymmetrical azine, acetophenone benzaldehyde azine, **12**, formed by dehydrogenation of (−)-(*S*)-**4**. Such a dehydrogenation reaction is also observed in the decomposition of 1,1′-diphenylazoethane in the presence of octanethiol in which acetophenone azine is formed (35). These dehydrogenations may be initiated by hydrogen abstraction from the azo compounds by thiyl radicals.



$$C_6H_5\text{—}C(CH_3)\text{=N—N=}CHC_6H_5$$

12

Two control experiments were carried out in an attempt to determine the amounts of racemization of starting material and product which might occur during decomposition of (−)-(*S*)-**4** in the presence of butanethiol. In the first a solution of optically pure (−)-(*R*)-**9** and 1,1′-diphenylazoethane in butanethiol was heated at 110° for a time equivalent to ~ 10 half lives of decomposition of the azo compound. Recovered (−)-(*R*)-**9** was 20% racemized. While 1,1′-diphenylazoethane and (−)-(*S*)-**4** decompose at somewhat different rates, the steady state concentration of butanethiyl radicals generated by the decomposing azo compounds should be closely similar in each case. The amount of racemization observed in the control experiment should represent an upper limit for the amount of racemization of (−)-(*R*)-**9** after its formation during the decomposition of (−)-(*S*)-**4** in butanethiol for two reasons. The concentration of (−)-(*R*)-**9** in the control experiment was already at its maximum value at the beginning of the reaction while during the decomposition of (−)-(*S*)-**4** it built up from 0. Since racemization is first order in both (−)-(*R*)-**9** and butanethiyl radicals, it proceeded at a faster rate in the control reaction during most of the run. Also, in butanethiol, (−)-(*S*)-**4** probably isomerizes to hydrazone much faster than does 1,1′-diphenylazoethane. Both azo compounds had probably completely disappeared as a result of decomposition and isomerization well before the reactions were stopped, but (−)-(*S*)-**4** disappeared faster. The result is that radicals were generated for a longer period of time in the control run, again giving more racemization of (−)-(*R*)-**9**.

In the second control run a decomposition of (−)-(*S*)-**4** in butanethiol at 110° was interrupted after a time equivalent to $\sim 20\%$ decomposition. The coupling product, (−)-(*R*)-**9**, which was isolated was 17.3% optically pure. This optical yield is identical to that from a run under the conditions which had gone to completion and shows that little, if any, racemization of (−)-(*R*)-**9** occurs after its formation. This also indicates that there is little, if any, racemization of (−)-(*S*)-**4** during its decomposition. The greater amount of racemization which was observed in the control run probably occurs for the reasons cited above.

Recovery of starting material from the interrupted reaction gave a mixture, $[\alpha]_D^{25}$ −101°, consisting of 71.5% (−)-(*S*)-**4** and 28.5% of the hydrazone, (−)-(*S*)-**2**, as determined by n.m.r. spectroscopy. On the assumption that the (−)-(*S*)-**2** present was optically pure the recovered azo compound would have $[\alpha]_D^{25}$ −114°, indicating that it was 25% racemized. This, however, represents an upper limit for the amount of racemization for racemic azo compound may have been introduced during workup. The unreacted azo compound was reduced with a 13-fold excess of diimide to the hydrazine which was then extracted into aqueous acid to free it from hydrazones, azine, and (−)-(*R*)-**9** which are also present in the reaction mixture. The hydrazine was liberated and oxidized back to the azo compound with oxygen. Diimide was used because it reduces azo compounds rapidly, it reduces polar double bonds such as are present in the hydrazones and azine more slowly (36), and because catalytic hydrogenation was precluded by the presence of sulfur compounds. It is possible that some reduction of acetophenone benzylhydrazone, if present, and azine, **12**, occurred. This would have resulted in the formation of racemic hydrazine, **3**, and, thus, racemic azo compound, **4**. The actual amount of racemization of (−)-(*S*)-**4**, may thus have been quite small, as was concluded above by comparing the optical yields of (−)-(*R*)-**9** isolated from the interrupted and completed runs.

Consideration of the stereochemistry of the decompositions in pure solvents in the absence of butanethiol also leads to the conclusion that there is little racemization of either starting material or product during decompositions in the presence of butanethiol. In chlorobenzene, for example, the cage effect in the decomposition of **4** is 33%. In the absence of hydrogen abstraction from starting material by the radicals which have escaped from the original solvent cage, the amounts of unsymmetrical coupling product formed from (−)-(*S*)-**4** inside and outside the original solvent cage would be equal.[6] That portion formed outside the original solvent cage will surely be racemic so that (−)-(*R*)-**9** formed by recombination within the original solvent cage would have twice the optical purity of the material actually isolated. The (−)-(*R*)-**9** isolated from a decomposition in pure chlorobenzene is 8.2% optically pure. That portion formed in the original solvent cage should then be 16.4% optically pure. This is greater than the 13% observed when the decomposition is carried out in the presence of 1.1 *M* butanethiol where only cage product is formed. It was shown from the dependence of product ratios upon initial concentration of **4** that a significant fraction of the radicals which escape from the original solvent cage do not give coupling products at the concentration used for decomposition of (−)-(*S*)-**4**. Less of the racemic coupling product would then be produced outside the original solvent cage. An accurate correction cannot be made for this effect, but any correction would be in a direction so as to make the stereochemistry of the cage recombination in pure chlorobenzene more similar to that in the presence of butanethiol.

Taken together, all the evidence indicates that any racemization of starting material or product during decomposition of (−)-(*S*)-**4** in the presence of butanethiol cannot be significant. The low optical yield of (−)-(*R*)-**9** from decomposition of (−)-(*S*)-**4** in the presence of butanethiol then must be almost entirely due to a racemization process taking place within the solvent cage after decomposition of (−)-(*S*)-**4** and before coupling of the radicals to (−)-(*R*)-**9**.

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[6] Of the ca. 67% of the coupling products which are formed outside the original solvent cage ca. 1/4 is bibenzyl, 1/4 is *meso*- + *dl*-**11**, and 1/2 is **9**.

Although the 1-phenylethyl radical must be either planar or very nearly so and rapidly inverting, it is in an asymmetric environment after it is generated as long as it remains in the original solvent cage (Chart V). Coupling product of inverted configuration can result from cage recombination only if the 1-phenylethyl radical rotates with respect to the benzyl radical before coupling with it. The relative rates of rotation, k_r, of the 1-phenylethyl radical with respect to the benzyl radical and of coupling k_c, of the two radicals within the solvent cage can be calculated with the information at hand. Chart V illustrates all the possible reactions of the caged radical pair. The 1-phenylethyl radical is assumed to be planar and the nitrogen molecule is not shown although it is present in the original solvent cage and must be displaced from between the radicals before they can couple. Equation [14] is derived by using the steady state assumption for the concentrations of the enantiomeric radical pairs within the original solvent cage. An expression for $(k_c/k_r)_{\text{cage}}$, eq. [15], can now be obtained using the relationships between k_c, k_{disp}, and k_{diff} which are given in eqs. [16] and [17]. F is the fraction of radicals which are consumed by coupling and disproportionation before diffusion from the original solvent cage and f is the fraction of radicals consumed in this way which undergo disproportionation. In general it will be assumed that the relative amount of disproportionation will be the same within and without the original solvent cage.

$$[14] \quad \frac{(-)\text{-}(R)\text{-}\mathbf{9}}{(+)\text{-}(S)\text{-}\mathbf{9}} = 1 + \left(\frac{k_c + k_{\text{disp}} + k_{\text{diff}}}{k_r}\right)_{\text{cage}}$$

$$[15] \quad (k_c/k_r)_{\text{cage}} = F(1-f)\left(\frac{(-)\text{-}(R)\text{-}\mathbf{9}}{(+)\text{-}(S)\text{-}\mathbf{9}} - 1\right)$$

$$[16] \quad \left(\frac{k_c + k_{\text{disp}}}{k_c + k_{\text{disp}} + k_{\text{diff}}}\right)_{\text{cage}} = F$$

$$[17] \quad \left(\frac{k_{\text{disp}}}{k_c + k_{\text{disp}}}\right)_{\text{cage}} = f$$

The two sets of values for $(k_c/k_r)_{\text{cage}}$ in Table IV, calculated assuming either 0 or 10% disproportionation, are very similar and show that the ratio, $(k_c/k_r)_{\text{cage}}$, is not very sensitive to reasonable errors (~ 10%) in the determination of the cage effect. Even within the original solvent cage the rate of rotation of the 1-phenylethyl radical with respect to the benzyl radical about any axis perpendicular to the line joining the two is much greater than its rate of coupling with the benzyl radical. The rate of such rotation of 1-phenylethyl radicals within the solvent cage is also found to be much greater than their rate of coupling during the decomposition of (−)-1,1′-diphenylazoethane in benzene at 110° (20). There

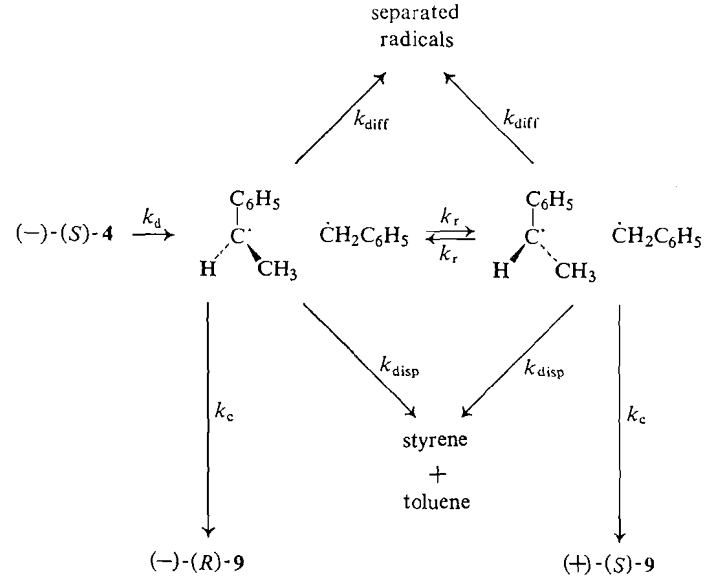
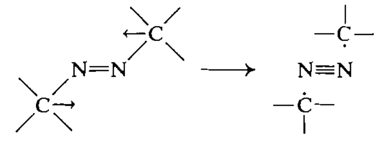


Chart V

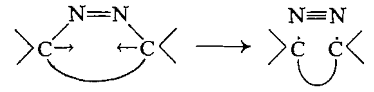
is no significant solvent effect on the ratio, $(k_c/k_r)_{cage}$.

This very small ratio of coupling to rotation contrasts dramatically with ratios of coupling to rotation found in studies of diradicals generated from cyclic precursors (6, 33) in which k_c/k_r can be greater than 50 (6*a*). This must be due to the position of the nitrogen atom in the solvent cage in the acyclic systems. Decomposition of acyclic azo compounds most probably occurs with the groups in the *trans* arrangement about the N=N bond. When formed the two radicals have a nitrogen molecule situated between them on the line joining them, eq. [18]. Numerous collisions may take place before the nitrogen molecule is displaced from this position allowing ample time for rotation to take place. Diradicals generated from the cyclic systems studied do not have any such molecules situated between them even when these are derived from azo compounds, eq. [19], and there is no such hindrance to coupling.

[18]



[19]



Even in acyclic systems there is a very large spread in the values of $(k_c/k_r)_{cage}$ among the only three systems already studied. In frozen solution $(k_c/k_r)_{cage}$ for the 3-methyl-2-phenyl-2-butyl radical pair, generated photochemically from either *meso*- or *dl*-3,3′-dimethyl-2,2′-diphenylazo-2-butane, appears to be as large as 50 (7), while for the 1-phenylethyl-benzyl radical pair in liquid solution at 110° it is as small as 0.060. This is a range of $\sim 10^3$ and leaves much room for further investigation.

The optically active esters obtained from decomposition of optically active diacyl peroxides are formed with very high (75–90%) retention of configuration in the alcohol part of the ester (4). On the basis of the results observed in the present study the very high degree of retention observed in the diacyl peroxide decompositions does not seem to be compatible with a process in which the ester is formed by the cage recombination of an acyloxy radical with an alkyl radical. The formation of the alkyl radical would have to be a two-step process proceeding via the acyloxy radical and the present results indicate that the orientation of the two acyloxy radicals with respect to one another must very rapidly become randomized. The original interpretation that ester does not arise by a free radical process (4*a*) thus gains added support, and it is likely that at least the majority of the ester is formed by an alternative route (3) which should give high retention.

Stereoselective cage recombinations of radicals are probably involved in other processes. The Wittig rearrangement of metallated benzyl ethers to benzyl carbinol salts proceeds with partial retention of configuration when optically active substrates are used (37) as does the Meisenheimer rearrangement (38). It now appears that stereoselective free radical cleavage – recombination processes are involved in both the Wittig (39, 40) and Meisenheimer (38, 41) rearrangements. The chromic acid oxidation of tertiary hydrocarbons to tertiary alcohols proceeds with a high degree of retention of configuration and it has been suggested that this reaction also proceeds by a free radical pathway involving stereoselective cage recombination (42). All three of these reactions proceed with a considerably higher degree of retention of configuration (~ 30 to ~ 100%) than is observed in the cage recombination of the radicals derived from (−)-(*S*)-**4**. In each of these reactions there is no hindrance to the recombination of the fragments as is provided by the nitrogen molecule during the decomposition of (−)-(*S*)-**4** so that a higher degree of retention might be expected. The formulation of these reactions as proceeding via radical intermediates is therefore entirely consistent with the results of the studies of decomposition of optically active azo compounds.

Experimental

All melting points and boiling points are uncorrected. Elemental analyses were performed by Mrs. Darlene Mahlow and Mrs. Andrea Dunn. Nuclear magnetic resonance (n.m.r.) spectra were recorded on a Varian A-60 analytical spectrometer using tetramethylsilane as internal standard. Unless otherwise specified spectra were taken of 10–20% w/v solutions in carbon tetrachloride. Infrared (i.r.) spectra were recorded on a Perkin–Elmer recording infrared spectrophotometer, model 421. Ultraviolet spectra were recorded on a Bausch and Lomb Spectronic 600 spectrophotometer. Optical rotations were measured with a Rudolph polarimeter, model 80, or with a Perkin–Elmer 141 polarimeter. Optical rotatory dispersion (o.r.d.) measurements were taken on a model ORD/uv-5 Japan Spectroscopic Company spectrophotometer. Gas–liquid chromatographic (g.l.c.) analyses were done with an Aerograph A90-P3 fractometer using helium as the carrier gas. Unless otherwise indicated a 6 ft × $\frac{1}{4}$ in. stainless steel column filled with 20% SF-96 on 60/80 Chromosorb P was used.

Solvents

Benzene, cumene, and cyclohexane were shaken with cold sulfuric acid until colorless, several times with water, and once with sodium carbonate solution. After drying over sodium carbonate the solvents were distilled from sodium through a short Vigreaux column and then redistilled through an annular Teflon spinning band distillation column. The middle fraction was taken and stored over sodium. Solvents were redistilled as required just before use. Chlorobenzene was purified in a similar manner except that the preliminary distillation was made over phosphorous pentoxide and it was stored over molecular sieves. Butanethiol was purified by distillation of commercial material, to which some sodium had been added, through a 6 in. Vigreaux column. This was stored for short periods in a brown bottle.

(–)-(S)-1-Phenylethylhydrazine, (–)-(S)-1

A mixture of 80 g (0.66 mole) of (–)-(*S*)-1-phenylethylamine (22) $[\alpha]_D^{25}$ –36.6° (neat, *l* 1 dm), 95% optically pure, and 500 ml water containing 25 g (0.45 mole) potassium hydroxide was stirred vigorously while a solution of 25 g (0.22 mole) freshly prepared (43) hydroxylamine-*O*-sulfonic acid dissolved in the minimum amount of water was added over a 30 min period (44). The temperature rose slowly to 50° during the addition. The reaction mixture was stirred for 2 h longer, cooled, and extracted twice with ether. The combined extracts were dried over sodium carbonate and then concentrated to an oil. The oil was distilled through a 6 in. Vigreaux column until most of the amine had distilled, b.p. 80–90° (25–35 mm), leaving a small amount of higher boiling material. The recovered amine was recycled through the reaction procedure twice more. Twenty-eight grams of starting material were recovered. The high boiling residues were combined and distilled twice through a 6 in. Vigreaux column. The fraction b.p. 70° (1 mm) was collected, 4.5 g (8%), n_D^{25} 1.5436, $[\alpha]_D^{25}$ –29.0° (*c*, 0.784, benzene). Reported (45) for (±)-**1**, b.p. 69° (0.8 mm), n_D^{25} 1.5436. A satisfactory rotation on the pure liquid could not be obtained as bubbles always formed in the polarimeter tube and variable readings were obtained.

Benzaldehyde 1-Phenylethylhydrazone, 2

To a stirred solution of 6.8 g (0.05 mole) 1-phenylethylhydrazine (45) in 80 ml ether were added 6 g anhydrous magnesium sulfate and, 5.5 g (0.052 mole) of freshly distilled benzaldehyde was then added over a period of 30 min. The resulting mixture was stirred overnight and filtered. The solvent was removed under reduced pressure to give a light-yellow oil. Pentane solutions of the oil deposited white crystals, m.p. 50–54°, whose melting point did not change upon recrystallization. Both the oil and the crystals had the same n.m.r. spectrum which showed absorption τ 2.5–3.1 (multiplet, 11.4 H), τ 4.6 (broad singlet, 0.93 H), τ 5.65 (quartet, *J* = 6.5 c.p.s., 0.93 H), and at τ 8.57 (doublet, *J* = 6.5 c.p.s., 3.0 H).

(+)-(R)-Benzaldehyde 1-Phenylethylhydrazone, (+)-(R)-2

(+)-(*R*)-1-Phenylethylamine (22), $[\alpha]_D^{25}$ +35.1° (neat, *l* 1 dm), 92% optically pure, was converted to (+)-(*R*)-**1** by the procedure used for the preparation of (–)-(*S*)-**1**. This was converted to (+)-(*R*)-**2**, using the procedure described for the preparation of **2**. After all traces of solvent were removed at reduced pressure (+)-(*R*)-**2** had $[\alpha]_D^{25}$ +63.5° (*c*, 3.31, benzene).

N-Benzyl-N′-(1-phenylethyl)-hydrazine, 3

A solution of hydrazone, **2**, prepared from 42 g of **1** was hydrogenated directly without removing the ether solvent with 5 g of 5% palladium-on-charcoal under an initial pressure of 50 lb hydrogen until uptake of hydrogen ceased. The mixture was filtered under an atmosphere of nitrogen and 39 g of oxalic acid dihydrate dissolved in the minimum amount of hot ethanol was added. An immediate precipitate formed. The mixture was filtered to give 72 g white crystals, m.p. 180–183° after 4 recrystallizations.

Anal. Calcd. for 1:1 base:acid, $C_{17}H_{20}N_2O_4$: C, 64.54; H, 6.40; N, 8.86.

Anal. Calcd. for 2:1 base:acid, $C_{32}H_{38}N_4O_4$: C, 70.82; H, 7.06; N, 10.32. Found: C, 66.30, 66.76; H, 6.58, 6.68; N, 9.63.

The results of the elemental analysis indicate that the salt has the approximate composition $(C_{15}H_{18}N_2)_{1.5}$ $C_2O_4H_2$.

The free hydrazine, **3**, was obtained by addition of 60 g of the recrystallized oxalate salt to an excess of aqueous potassium hydroxide. The aqueous layer was extracted several times with methylene chloride and the combined organic layers were dried over sodium carbonate. After removal of the solvent under reduced pressure the residual oil was distilled to give 41.8 g of a colorless liquid, b.p. 135° (0.5 mm), n_D^{25} 1.5685. All operations were carried out under an atmosphere of nitrogen. The n.m.r. spectrum of **3** showed absorption at τ 2.83 (2 over-lapping singlets, 10 H), τ 6.16 (quartet, *J* = 7.0 c.p.s.) over-lapping with absorption at τ 6.28 (singlet) due to the hydrogens of the methylene group, (combined area 3.07 H), τ 6.95 (singlet, 2.0 H), and at τ 7.89 (doublet, *J* = 7.0 c.p.s., 2.94 H).

This material was very sensitive to air oxidation and a satisfactory elemental analysis was not obtained.

1,1′-Diphenyl-1-methylazomethane, 4

Solutions of **3** in ether were allowed to stand under an initial pressure of 10 lb oxygen until oxygen uptake stopped. The ether solution was shaken several times with water and dried over sodium carbonate. The ether was removed under reduced pressure using a rotary evaporator and evaporation continued until there was no further change in refractive index. Yields were quantitative, n_D^{25} 1.5598; λ_{max} (benzene) 358 mμ (ε 51). The n.m.r. spectrum showed absorption at τ 2.80 (multiplet, 10.6 H), τ 5.18 (singlet, ~ 2H) over-lapping with absorption at τ 5.42 (quartet, *J* = 7.0 c.p.s., ~ 1H) (combined area 2.90 H), and at τ 8.50 (doublet, $J = 7.0$ c.p.s., 3.10 H).

Anal. Calcd. for $C_{15}H_{16}N_2$: C, 80.32; H, 7.19; N, 12.49. Found: C, 80.21; H, 6.99; N, 12.67.

(−)-(S)-1,1′-Diphenyl-1-methylazomethane, (−)-(S)-4

A Via Resolution of 3

A solution of 96 g (0.48 mole) of *d*-camphoric acid in 300 ml ethyl acetate was added to a solution of 108 g (0.51 mole) of **3** dissolved in 325 ml dioxane. The mixture was allowed to stand overnight at 25° and the precipitate which formed was filtered and washed with ether to give 115 g of white crystals, $[\alpha]_D^{25}$ +11.2° (*c*, 3.8, methanol). This material was recrystallized twice: first recrystallization, 55 g, $[\alpha]_D^{25}$ +2.73° (*c*, 3.3, methanol); second recrystallization, 30 g, m.p. 95–105° $[\alpha]_D^{25}$ −2.50° (*c*, 2.5, methanol). Further recrystallization did not alter the rotation or the melting point. The salt could be stored indefinitely at 0° but decomposed slowly at 25°.

The twice crystallized camphorate salt was added to excess aqueous sodium bicarbonate and the resulting oil extracted into ether. The hydrazine was usually not isolated but was converted to the corresponding azo compound by the oxidation procedure described above, $[\alpha]_D^{25}$ −152° (*c*, 1.06, benzene). Material obtained from a second resolution had $[\alpha]_D^{25}$ −150° (*c*, 1.1, benzene). Optical rotatory dispersion (*c*, 0.0179, cyclohexane): $[\Phi]_{600}$ −209°, $[\Phi]_{500}$ −377°, $[\Phi]_{450}$ −628°, $[\Phi]_{400}$ −1676°, $[\Phi]_{380}$ −2528°, $[\Phi]_{354}$ ±0°, $[\Phi]_{350}$ +726°, $[\Phi]_{330}$ +2095°, $[\Phi]_{320}$ +1732°.

Samples of (−)-(*S*)-**3** which were isolated by evaporation of solvent exhibited a negative rotation which varied widely from run to run.

B From (−)-(S)-1

In another experiment a mixture made up from 2.2 g (0.016 mole) of (−)-(*S*)-**1**, prepared from (−)-(*S*)-**5** of $[\alpha]_D^{25}$ −36.6° (neat, *l* 1 dm), 95% optically pure, 1 g magnesium sulfate, and 2.1 g (0.019 mole) benzaldehyde in 10 ml benzene was allowed to stand several hours. The reaction mixture was then filtered and 40 ml of a 25% solution of diisobutylaluminium hydride in benzene were added dropwise to the stirred filtrate under a nitrogen atmosphere. The addition required 30 min. The reaction mixture, which had become warm, was stirred at 25° for 2 days and then cooled in an ice bath. A solution of benzene–methanol (1:1) was added dropwise until there was no vigorous reaction on further addition. This was followed by the addition of 5 ml water, 10 ml 15% potassium hydroxide, and then 5 ml water. The aqueous layer was extracted with ether. The organic fractions were combined, dried over sodium carbonate, and poured into a solution of 2.6 g oxalic acid dihydrate in 10 ml of 98% ethanol. A white precipitate formed immediately. The mixture was allowed to stand at 0° for several hours and then filtered. The crystals, 1.9 g, were recrystallized from ethanol and the resulting solid, 1.5 g, was converted to the free hydrazine, (−)-(*S*)-**3**, as described previously. This material was not isolated but was oxidized directly to the azo compound as described above. The product after removal of the ether using a rotary evaporator contained 7.5% of (−)-(*S*)-**1**, by n.m.r. analysis, and had $[\alpha]_D^{25}$ −140° (*c*, 1.36, benzene). No other absorptions could be found. On the basis that the (−)-(*S*)-**1** present had $[\alpha]_D^{25}$ −28° and has the same density as (−)-(*S*)-**4**, (−)-(*S*)-**4** in the mixture has $[\alpha]_D^{25}$ −146°. Optically pure (−)-(*S*)-**4** would then have $[\alpha]_D^{25}$ −153°.

Hydrogenolysis of (−)-(S)-4

A mixture of 1.7 g (−)-(*S*)-**4**, $[\alpha]_D^{25}$ −152° (*c*, 1.06, benzene), 2 g Raney nickel, and 40 ml methanol was stirred at 25° in a microhydrogenation apparatus at atmospheric pressure. One equivalent of hydrogen was taken up within a few minutes and a second equivalent after two days. Analysis by g.l.c. showed that the main products were benzylamine and (−)-(*S*)-**5** together with small amounts of toluene and ethylbenzene. The mixture was filtered and the filtrate concentrated to a small volume. The residual oil was injected in 100 µl portions into the SF-96 g.l.c. column operating at 160° with a flow rate of 150 ml/min of helium. Partial separation of the amines was achieved in this way.

Material rich in (−)-(*S*)-**5** was collected from the effluent stream. Recycling of this material afforded 55 mg of pure (g.l.c.) (−)-(*S*)-**5**, $[\alpha]_D^{25}$ −31.4° (*c*, 5.4, dioxane). Optically pure (−)-(*S*)-**5** is calculated from literature data (46, 22) to have $[\alpha]_D^{25}$ −39.6° under these conditions.

In a control experiment 2 g of (−)-(*S*)-**5**, $[\alpha]_D^{25}$ −36.6° (neat, *l* 1 dm), in 40 ml methanol was stirred under the above hydrogenolysis conditions with 2 g Raney nickel for three days. The recovered amine had n_D^{25} 1.5245, $[\alpha]_D^{25}$ −36.5° (neat, *l* 1 dm).

2,3-Diphenyl-1-propanol, 7

A solution of 11 g (0.049 mole) of 2,3-diphenylpropionic acid, **6**, in 100 ml ether was added slowly to a slurry of 4.75 g (0.125 mole) of lithium aluminium hydride in 180 ml ether. The reaction mixture was stirred overnight and then hydrolyzed by the addition of water, followed by sulfuric acid. The ether layer was shaken twice with aqueous sodium carbonate, dried over sodium carbonate, and concentrated. Distillation of the residue gave 6.0 g (60%) of a light yellow oil, b.p. 140° (0.4 mm), n_D^{25} 1.5758; reported (47) b.p. 300–302°. The n.m.r. spectrum showed absorption at τ 2.95 (multiplet, 10.0 H), τ 6.3–7.4 (broad multiplet, 5.0 H), and at τ 8.05 (singlet, 1.1 H).

(−)-(R)-2,3-Diphenylpropanol, (−)-(R)-7

Using the above procedure, (−)-(*R*)-**6** (28), $[\alpha]_D^{25}$ −132° (*c*, 0.062, chloroform), 100% optically pure, was converted to (−)-(*R*)-**7**, n_D^{25} 1.5745, $[\alpha]_D^{25}$ −88.5° (*c*, 1.08, chloroform). Reported (25) for (+)-(*S*)-**7**, n_D^{25} 1.5742, $[\alpha]_D^{25}$ +76.3° (*c*, 5.3, chloroform).

2,3-Diphenyl-1-propyl p-Toluenesulfonate, 8

This material was prepared from **7** by the procedure of Schleyer (48), m.p. 79.5–89.5° after recrystallization from ligroin.

Anal. Calcd. for $C_{22}H_{22}O_3S$: C, 72.10; H, 6.05; S, 8.75. Found: C, 72.34; H, 5.88; S, 8.96.

(−)-(R)-2,3-Diphenyl-1-propyl p-Toluenesulfonate, (−)-(R)-8

This material was prepared from (−)-(*R*)-**7**, $[\alpha]_D^{25}$ −88.5°, 100% optically pure, by the above procedure, m.p. 91.0–93.5°, $[\alpha]_D^{25}$ −42.6° (*c*, 0.51, chloroform); reported (25) for (+)-(*S*)-**8**, m.p. 89–90°, $[\alpha]_D^{25}$ +40.2° (*c*, 2.4, acetone).

(−)-(R)-1,2-Diphenylpropane, (−)-(R)-9

A solution of 0.40 g of (−)-(*R*)-**8**, $[\alpha]_D^{25}$ −42.6°, 100% optically pure, in 15 ml ether was added dropwise to a slurry of 1.0 g lithium aluminium hydride in 40 ml ether. The reaction mixture was stirred for two days at 25°. It was hydrolyzed by adding ice water and then 6 *N* hydrochloric acid dropwise. The ether layer was dried over sodium carbonate and then concentrated to an oil. Analysis by g.l.c. showed only one product which was collected from the effluent stream, 0.074 g (30%), m.p. 22.0–23.0°, n_D^{25} 1.5572, $[\alpha]_D^{25}$ −80.5° (*c*, 3.2, chloroform). Optical rotatory dispersion (*c*, 1.54, cyclohexane): $[\Phi]_{600}$ −167°, $[\Phi]_{450}$ −333°, $[\Phi]_{350}$ −833°, $[\Phi]_{300}$ −1666°, $[\Phi]_{280}$ −2666°.

The g.l.c. retention time of this material was identical with a sample of **9** (49) prepared by the hydrogenation of α-methylstilbene; reported (25) for (−)-(*R*)-**9**, n_D^{25} 1.5553, $[\alpha]_D^{25}$ −76.3° (*c*, 2.2, chloroform), for (+)-(*S*)-**9**, n_D^{25} 1.5558, $[\alpha]_D^{25}$ +76.7° (*c*, 2.3, chloroform).

1,1′-Diphenylazoethane

This material was prepared by the published procedure (18*b*) except that the oxidation of the corresponding hydrazone was carried out with oxygen as described for the preparation of **4**, m.p. 68–71°; reported (18*b*), m.p. 72.3–72.9°.

Kinetic Studies

The rates of evolution of nitrogen from solutions of **4** (~ 0.1–0.2 *M*) in cumene were measured using an apparatus and a procedure similar to that described by Peterson(50). Rate constants were determined from the initial slopes of plots of log $(V_\infty - V_0/V_\infty - V_t)$ vs. time using the theoretical value of V_∞. V_0 was determined as described by Petersen *et al.* (50). The results are summarized in Table I.

Product Studies

For quantitative analyses solutions of **4** were placed in Pyrex tubes, degassed by several freeze-thaw cycles, and then heated at the appropriate temperature for at least 6 half-lives after the tubes were sealed. After cooling to −78° the tubes were opened and the solutions analyzed directly by temperature-programmed g.l.c. The temperature of the column was raised from 100 to 200° over a 35 min period beginning immediately after injection. The helium flow rate was 50 ml/min.

Hydrocarbon products were identified by comparison of g.l.c. retention times with those of authentic samples, and in the cases of bibenzyl, **9** and *meso*- and *dl*-**11** also by comparison of the n.m.r. spectra of isolated materials with those of authentic samples. The order of elution of the higher molecular weight products was bibenzyl, **9**, *dl*-**11**, and *meso*-**11**. Authentic samples of *meso*- and *dl*-**11** were prepared by the method of Barber *et al.* (51). Relative thermal response factors for the hydrocarbons were determined to be: toluene, 55; ethylbenzene, 60; bibenzyl, 85; **9**, 100; and *meso*- and *dl*-**11**, 95.

In preparative runs solutions of 1–2 g of (±)-**4** or optically pure (−)-(*S*)-**4** in 20–50 ml of solvent were placed in a 75 ml stainless steel bomb, flushed several minutes with nitrogen, and heated at the appropriate temperature for at least 7 half-lives. Most of the solvent was then removed through the spinning band column. When butanethiol was not present, the products were isolated from the residual oil by temperature-programmed preparative g.l.c. using the above conditions. When butanethiol was present in solution by-products formed which were eluted slowly from the g.l.c. column and repetitive injections of the residual oil could not be made. In these cases the by-products were removed by adsorbing the residual oil on a 5 cm × 40 cm column of activated basic alumina and eluting the hydrocarbon present with 200 ml hexane. After concentration of the hexane eluent through the spinning band column (±)-**9** or (−)-(*R*)-**9** were isolated from the residual oil by preparative g.l.c. using a steady column temperature of 205°. Amounts of (±)-**9** or (−)-(*R*)-**9** obtained, ranged from 10 to 100 mg. The smaller amounts were obtained when the sample had some impurities present after the first g.l.c. pass and had to be recycled.

From decompositions of (−)-(*S*)-**4** carried out in pure butanethiol as solvent, a yellow solid could be isolated which has a g.l.c. retention time very similar to that of (−)-(*R*)-**9**. It was not investigated further but is presumed to be the mixed azine of acetophenone and benzaldehyde. Smaller amounts of this yellow material were formed in decomposition in 1 *M* butanethiol.

Control Experiments

A Racemization of (−)-(R)-9 in Butanethiol

A solution made up of 1.2 g of 1,1′-diphenylazoethane, 36 ml butanethiol, and 80 mg of optically pure (−)-(*R*)-**9**, $[\alpha]_D^{25}$ −80.5° (*c*, 3.2, chloroform), was heated in the bomb at 110° for 12 h (~ 10 half-lives of decomposition of the azo compound); recovered (−)-(*R*)-**9** had $[\alpha]_D^{25}$ −64.1° (*c*, 1.42, chloroform).

B Interrupted Decomposition of (−)-(S)-4

A solution of 2.0 g optically pure (−)-(*S*)-**4** in 30 ml butanethiol was heated in the bomb at 110° for 5 h (~ 20% decomposition). Butanethiol was removed under reduced pressure and the residue was taken up in 50 ml methanol. Twenty grams of potassium azodicarboxylate were added, followed by the dropwise addition of acetic acid until the reaction mixture became colorless. Ether, 100 ml, was added and the resulting mixture was shaken with dilute sulfuric acid. The aqueous layer was shaken several times with ether, made alkaline with dilute potassium hydroxide solution, and shaken twice with ether. The latter ethereal extracts were combined, allowed to stand under an atmosphere of oxygen for several hours, shaken with water, and then dried over sodium carbonate. Removal of the ether gave a small amount of an oil $[\alpha]_D^{25}$ −101° (*c*, 1.3, benzene). The n.m.r. spectrum of this oil showed it to be a mixture of (−)-(*S*)-**4**, 71.5% and of (−)-(*S*)-**2**, 28.5%. No absorptions other than those due to these materials could be detected. On the basis that the (−)-(*S*)-**2** present is optically pure and has $[\alpha]_D^{25}$ −69°, the rotation of the recovered azo compound would be $[\alpha]_D^{25}$ −114°.

The ether layer remaining after the extraction with sulfuric acid was concentrated to an oil. The oil was chromatographed on alumina and the hydrocarbon, (−)-(*R*)-**9**, 0.012 g, isolated from the concentrated eluent by g.l.c. had $[\alpha]_D^{25}$ −13.9° (*c*, 1.2, chloroform).

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