Stereochemistry of Free-Radical Recombination Reactions. The Cage Effect in Decomposition of *SS*-(−)-Azobis-α-phenylethane[1a,b]

Frederick D. Greene, Martin A. Berwick,[1c] and John C. Stowell[1d]

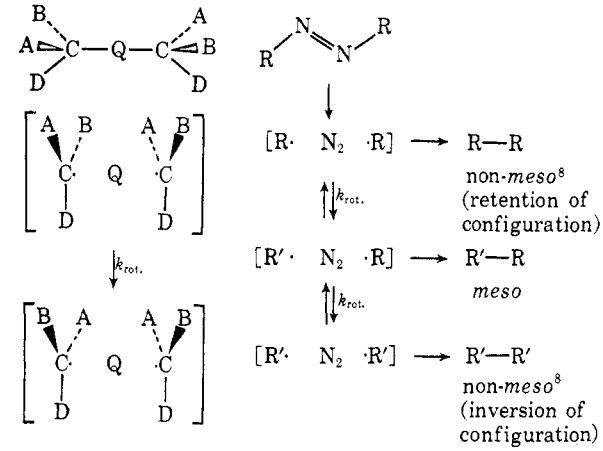
Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received August 4, 1969*

Abstract: The thermal decomposition of optically pure *SS*-(−)-azobis-α-phenylethane [*SS*-(−)-1,1′-diphenylazoethane] and the corresponding *meso*-azo compound in benzene at 105° has been examined in the presence and absence of scavengers (2-methyl-2-nitrosopropane and thiophenol). In the absence of scavengers, both *meso*-azo and non-*meso*-azo gave nearly equal amounts of *meso* and non-*meso*-2,3-diphenylbutane in an over-all yield of 88 ± 2%. The cage effect from optical activity data and from yield data is 32 ± 2%. Decomposition of the *SS*-(−)-azo compound in benzene in the presence of 2-methyl-2-nitrosopropane affords *meso* and non-*meso*-2,3-diphenylbutane (*meso*, 48.1%; non-*meso* of retained configuration, 31.3%; non-*meso* of inverted configuration, 20.6%). Recombination of statistically distributed α-phenylethyl radicals, generated by *t*-butoxyl radical attack on ethylbenzene, proceeds with no stereoselectivity. The stereochemical results of the decomposition of *SS*-(−)-azo compound indicate that considerable randomization of orientation of the α-phenylethyl radicals relative to each other in the solvent cage occurs prior to recombination. An analysis is presented in terms of the competing processes available to the radical pair: $k_{diffusion}$, $k_{combination}$, $k_{disproportionation}$, and $k_{rotation}$ [180° change in orientation (by out-of-plane rotation) of one α-phenylethyl radical relative to the other α-phenylethyl radical of the "caged" pair]; $k_{rotation}/(k_{diffusion} + k_{combination} + k_{disproportionation}) = 4.1$; relative k's—combination (1.0), disproportionation (0.14), diffusion (2.4), rotation (15). The relationship of the results of this study to other cases is discussed with respect to the nature of the radical, radical geometry, and to the role of the intervening nitrogen molecule in [R · N_2 · R] on the cage recombination.

Stereoselectivity[2] in free-radical atom transfer reactions is well documented.[3] Stereospecificity[2] in such reactions is restricted to a few rather special systems,[4] *e.g.*, the 9-decalyl,[4a,b] the lack of stereospecificity in radical atom transfer reactions being due to the general inability of carbon radicals to hold configuration.[4,5] The question of structure of a carbon radical,[6] planar *vs.* rapidly inverting pyramid, has not been fully resolved although the available evidence strongly supports the planar structure for the methyl radical[6a,b] and favors this structure for other radicals with the exception of the fluoroalkyl radicals,[6c,d] vinyl radicals,[5] cyclopropyl radicals,[6e] and possibly, oxygen-substituted radicals.[6b]

Homolytic decomposition of a molecule necessarily generates the two odd-electron species in close proximity. These fragments then either diffuse away from each other or interact within the solvent cage[7] by disproportionation or recombination. If the substrate is optically active, then the radical pair assembly is also optically active at the instant of formation even though each radical may be planar. The assembly remains optically active until one of the radicals undergoes a 180° out-of-plane rotation relative to its partner (Scheme I).

Scheme I



(1) (a) Financial support from the Atomic Energy Commission [Contract No. AT(30-1)-905] is gratefully acknowledged; (b) presented at the 156th Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, Abstracts Orgn 112; (c) Ph.D. Thesis, M.I.T., May 1968; (d) Ph.D. Thesis, M.I.T., Aug 1964.

(2) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 434–436; see also H. E. Zimmerman, L. Singer, and B. S. Thyagarajan, *J. Am. Chem. Soc.*, **81**, 108 (1959), footnote 16.

(3) *E.g.*, see F. R. Jensen, L. H. Gale, and J. E. Rodgers, *ibid.*, **90**, 5793 (1968), and references cited therein.

(4) (a) P. D. Bartlett, R. E. Pincock, J. H. Rolston, W. G. Schindel, and L. A. Singer, *J. Am. Chem. Soc.*, **87**, 2590 (1965); (b) F. D. Greene and N. N. Lowry, *J. Org. Chem.*, **32**, 875 (1967); (c) P. S. Skell, D. L. Tuleen, and P. D. Readio, *J. Am. Chem. Soc.*, **85**, 2849 (1963); (d) W. O. Haag and E. I. Heiba, *Tetrahedron Lett.*, 3679, 3683 (1965); (e) H. M. Walborsky and C. J. Chen, *J. Am. Chem. Soc.*, **89**, 5499 (1967).

(5) L. A. Singer and N. P. Kong, *ibid.*, **89**, 5251, 6805 (1967); R. M. Kopchik and J. A. Kampmeier, *ibid.*, **90**, 6733 (1968).

(6) (a) D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **47**, 5146 (1967); L. Y. Tan and G. C. Pimentel, *ibid.*, **48**, 5202 (1968); M. T. Rogers and L. D. Kispert, *ibid.*, **46**, 221 (1967); (b) R. W. Fessenden, *J. Phys. Chem.*, **71**, 74 (1967); (c) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **43**, 2704 (1965); G. A. Carlson and G. C. Pimentel, *ibid.*, **44**, 4053 (1966); (d) T. Ando, F. Namigata, H. Yamanaka, and W. Funasaka, *J. Am. Chem. Soc.*, **89**, 5719 (1967); (e) see ref 4e, 6d, and references cited therein.

(7) See the following papers and references cited therein: (a) P. D. Bartlett and J. M. McBride, *Pure Appl. Chem.*, **15**, 89 (1967); (b) T. Koenig and M. Deinzer, *J. Am. Chem. Soc.*, **90**, 7014 (1968); T. Koenig, *ibid.*, **91**, 2558 (1969); T. Koenig and R. Wolf, *ibid.*, **91**, 2574 (1969); (c) J. C. Martin and S. A. Dombchik, Advances in Chemistry Series, No. 75, American Chemical Society, Washington, D. C., 1968, p 269; J. W. Taylor and J. C. Martin, *J. Am. Chem. Soc.*, **89**, 6904 (1967); (d) S. A. Weiner and G. S. Hammond, *ibid.*, **91**, 986 (1969); H. P. Waits and G. S. Hammond, *ibid.*, **86**, 1911 (1964); (e) O. Dobis, J. M. Pearson, and M. Szwarc, **90**, 278 (1968); K. Chakravorty, J. M. Pearson, and M. Szwarc, *ibid.*, **90**, 283 (1968); (f) H. Kiefer and T. G. Traylor, *ibid.*, **89**, 6667 (1967).

In this study, we have sought to elucidate the degree of freedom of a pair of radicals by examination of an optically active symmetrical azo compound, *SS*-(−)-azobis-α-phenylethane [*SS*-(−)-1,1′-diphenylazoethane], eq 1. The use of an azo compound with two asymmetric centers rather than with a single asymmetric center provides both the difficulty that rotation within the cage will lead to two combination products, non-*meso*[8] and *meso*, and the advantage of the additional information and internal check on mechanism provided by the possibility to analyze for all three species: non-*meso*[8] product of retained configuration, non-*meso*[8] product of inverted configuration, and *meso* product.

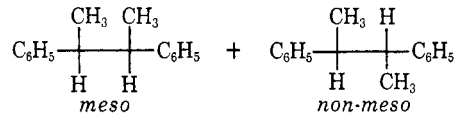
A study parallel to that of this paper, the thermal decomposition of the optically active unsymmetrical azocompound, 1,1′-diphenyl-1-methylazomethane, recently has been described.[9] The results of the two studies are in close agreement.

Results

Combination of Statistically Distributed α-Phenylethyl Radicals. The radicals were generated by the action of *t*-butoxyl radicals on ethylbenzene (Table I).

Table I

$C_6H_5CH_2CH_3$ + peroxide ⟶



Peroxide	Temp, °C	*meso*,[a] %	Non-*meso*,[a] %
Di-*t*-butyl peroxide	105	50	50
Di-*t*-butyl diperoxyoxalate	30	50	50

[a] ±1%.

Several possible products, derivable from coupling at positions other than the benzylic positions, were prepared [1,3-diphenylbutane, 4,4′-diethylbiphenyl, and 1-(4-ethylphenyl)-1-phenylethane]. No evidence for these was found from the radical coupling reaction;[10] the only dimeric products observed were *meso*- and *dl*-2,3-diphenylbutane, separable by glpc. As shown in Table I, there is no stereoselectivity in the combination step; $\Delta\Delta G^{\pm} = \Delta\Delta H^{\pm} = \Delta\Delta S^{\pm} = 0$ for the recombination of statistically distributed α-phenylethyl radicals. The method of analysis for *meso* and non-*meso* in Table I could have detected a difference, $\Delta\Delta G°$, 14–20 cal/mole.

Efforts to effect equilibration of the *meso* and non-*meso* compounds under the experimental conditions were unsuccessful. Equilibration was possible in di-*n*-butylamine with potassium[11] (Table II).

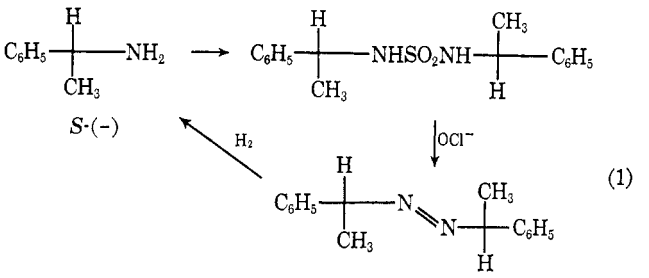
Table II[a]

Non-*meso*-2,3-diphenylbutane ⇌ *meso*-2,3-diphenylbutane

Temp, °C	*K*	$\Delta G°$, cal
49.6	2.39 ± 0.04	−560
80.1	2.14 ± 0.01	−535
126.5	1.87 ± 0.02	−494

$\Delta H° = -866 \pm 12$ cal, $\Delta S° = 0.94$ eu.

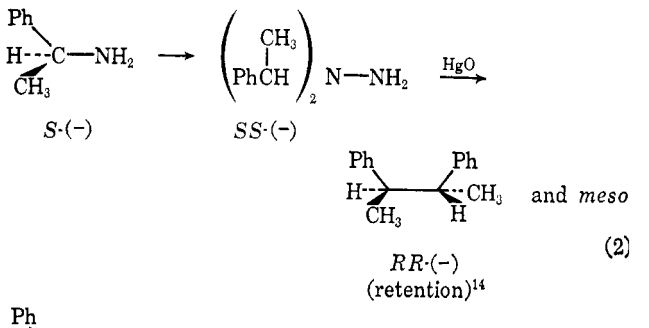
Cage Recombination of α-Phenylethyl Radicals. Syntheses and Configurational Assignments. Hydrogenolysis of *SS*-(−)-azo compound regenerated *S*-(−)-amine with 98% of its original rotation.[12] The previously known *meso*-azo compound, mp 71–72°, was prepared from acetophenone.



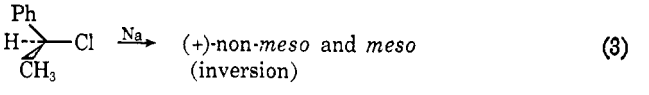
(1)

The major products of decomposition of either the *SS*- or the *meso*-azo compound are approximately equal amounts of *meso*- and non-*meso*-2,3-diphenylbutane. From *SS*-(−)-azo compound, the non-*meso* product was levorotatory. Resolution of this compound has been effected by two groups[13] with two different resolving agents, obtaining material of $[\alpha]^{25}D$ +98.9° and $[\alpha]^{20}D$ +95.7°, respectively. We assume the higher value represents optically pure material.

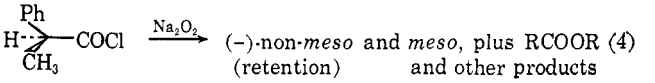
The *RR* configuration[14] is assigned to the (−)-non-*meso*-2,3-diphenylbutane on the basis of eq 2,[13b] 3,[15a] and 4.[15b]



(2)



(3)



(4)

(8) We use the descriptions "*meso*" and "non-*meso*" rather than "*meso*" and "*dl*" for the diastereomers since the latter compound will be of varying degree of optical purity in this report.

(9) K. R. Kopecky and T. Gillan, *Can. J. Chem.*, **47**, 2371 (1969).

(10) *I.e.*, if such coupling products were formed, they must have undergone reversal or further reaction faster than prototropic rearrangement to the new aromatic systems. For evidence on the formation of unsymmetrical coupling products (~2%) from cumyl radicals, see S. F. Nelson and P. D. Bartlett, *J. Am. Chem. Soc.*, **88**, 137 (1966).

(11) D. Y. Curtin, H. Gruen, Y. G. Hendrickson, and H. E. Knipmeyer, *ibid.*, **83**, 4838 (1961).

(12) After correcting for approximately 5.5% racemization of the amine under the hydrogenolysis conditions.

(13) (a) H. H. Richmond, E. J. Underhill, A. G. Brook, and C. F. Wright, *J. Am. Chem. Soc.*, **69**, 937 (1947); (b) C. G. Overberger, N. P. Marullo, and R. G. Hiskey, *ibid.*, **83**, 1374 (1961).

(14) The formation of *RR* product from *SS* reactant corresponds to *retention of configuration*, since this reaction exchanges the group of highest priority under the *RS* system of nomenclature, –N=N–, for the $C_6H_5CH(CH_3)$– group which is of lower priority than the C_6H_5– group.

(15) (a) E. Ott, *Chem. Ber.*, **61**, 2139 (1928); E. LeGoff, S. E. Ulrich, and D. B. Denney, *J. Am. Chem. Soc.*, **80**, 622 (1958); (b) F. D. Greene, *ibid.*, **77**, 4869 (1955).

Table III. Decomposition of Azobis-α-phenylethane

Azo	Scavenger	Time, hr	—2,3-Diphenylbutanes— Total, %[a]	Non-*meso*/*meso*[b]
In Benzene at 105°				
meso	None	36	88	0.99
SS-(−)	None	36	88	1.01
meso	*t*-BuNO[c]	3	28	0.92
meso	*t*-BuNO[d]	3	30	0.92
meso	*t*-BuNO	14	23	
meso	*t*-BuNO	1.5	28	
SS-(−)	*t*-BuNO[e]	3	28	1.05
meso	PhSH	36	*f*	0.89
SS-(−)	PhSH	36	*f*	1.11
meso	ArOH[g]	36	~100[h]	
Other conditions				
meso[i]	PhSH	36	*f*	0.92
meso[j]	PhSH	36	*f*	0.86
meso[k]	None	4	~5	0.26
meso[l]	None	24	40	0.98

[a] ±2. [b] ±0.03. [c] Concentration, 0.7 *M*. [d] Concentration, 1.4 *M*. [e] Concentration, 1.15 *M*. [f] Some destruction of reactant by scavenger. [g] 2,6-Di-*t*-butylphenol. [h] See ref 16. [i] Solvent, n-C_6H_{14}. [j] Solvent, $PhNO_2$. [k] *hν* −196°, in n-C_6H_{14}. [l] *hν* 32° in C_6H_6.

Stereochemistry of Radical Recombination. Decompositions of *meso*- and *SS*-(−)-azo compound were carried out in the presence and absence of scavengers (Table III). The best scavengers were 2-methyl-2-nitrosopropane and thiophenol.[16] With the latter there was some attack on reactant. Both *meso*- and non-*meso*-azo compound afford similar amounts of the *meso* and non-*meso*-2,3-diphenylbutanes, with yields of 88% in the absence of scavenger. The remaining 12% is ascribed to disproportionation to afford styrene and ethylbenzene. The presence of the nitroso scavenger drops the yield of butanes to a limiting value of 28 ± 2%, representing the amount of radical combination occurring before diffusion out of the original cages. The ratios of *meso* to non-*meso* dimer formed in the original cages is still close to the 1:1 value found in the absence of scavengers, indicating that extensive changes in orientations of the radicals are occurring in these original cages prior to radical recombination.

The results on the optical state of the non-*meso* dimer are summarized in Table IV; the stereochemical results are summarized in Table V.

Table IV

SS-(−)-azo-α-phenylethane $\xrightarrow[105°]{C_6H_6}$ *meso* and non-*meso* dimers

Scavenger	$[\alpha]^{25}D$ for the non-*meso* dimer, deg	% retention of configuration
None	−6.8	6.9
t-Butyl-NO	−20.1 ± 0.6	20.3
C_6H_5SH	−20.4 ± 0.6	20.6

(16) Experiments with 2,4,6-tri-*t*-butylphenol as scavenger afforded quantitative yields of the 2,3-diphenylbutanes, apparently due to reversal of the scavenging step.

$$PhCHCH_3\cdot + HOAr \rightleftharpoons PhCH_2CH_3 + \cdot OAr$$
$$\downarrow$$
$$PhCHCH_3CHCH_3Ph$$

Galvinoxyl, Koelsch radical, and tri-*n*-butyltin hydride were not suitable scavengers.

Table V. Distribution of Diastereomeric Products from *SS*-(−)-Azobis-α-phenylethane in Benzene at 105°

Recombination reaction	—% 2,3-diphenylbutanes, ±1%— *RR*[a]	*SS*[a]	*meso*
Original "cages"	31.3[b]	20.6[b]	48.1[b]
After diffusion	25	25	50

[a] Formation of *RR* product from *SS* reactant corresponds to retention of configuration (ref 14). [b] By use of the average values of 1.08 ± 0.04 for the non-*meso*/*meso* product ratio and 20.4 ± 0.6 for per cent retention of configuration of non-*meso* product (79.6% racemization).

The data of Tables III and IV provide two measures of the cage effect (fraction of recombination plus disproportionation occurring before diffusion of original partners): for both *meso*-azo and non-*meso*-azo compounds (from the yield data of Table III), 32 ± 2%,[17a] for non-*meso*-azo (from the optical data of Table IV), 32 ± 2%.[17b] A previous report has provided an estimate of the cage effect for *meso*-azo of 29% by a mass spectral method.[17c]

Control Experiments. Stability of reactant azo was shown by recovery of azo after partial reaction with negligible loss in optical activity. Stability of the product 2,3-diphenylbutanes was shown by the experiments of eq 5 and 6. Stability of the ethylbenzene (product of disproportionation) was shown by the experiment of eq 7.

azo compound + *meso*-$PhCH(CD_3)CH(CD_3)Ph$ → (C_6H_6) <0.2% D_6 in the non-*meso* dimer; (C_6H_5SH or *t*-butyl-NO) <1% D_6 in the non-*meso* dimer (5)

azo compound $\xrightarrow[C_6H_6]{C_6H_5S\cdot D}$ <2% D in dimers (6)

azo compound + $C_6H_5CH_2CD_3$ $\xrightarrow[C_6H_6]{C_6H_5SH}$ No D in dimers (7)

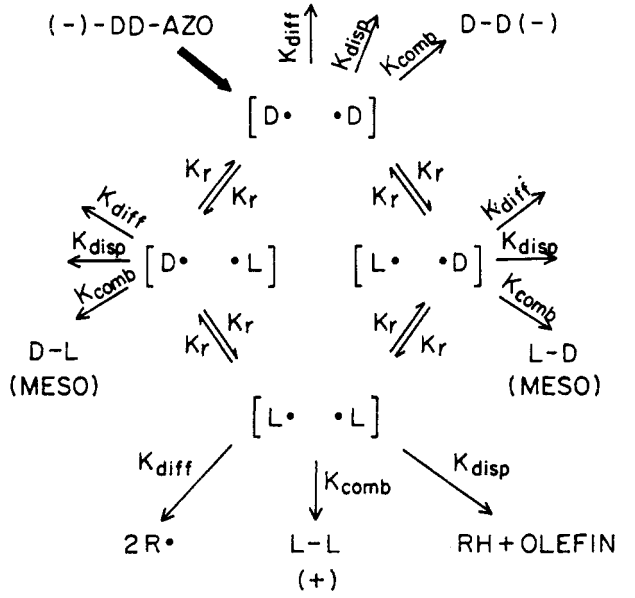
Discussion

The principal finding of this study, summarized in Tables III–V, is that a good deal of randomization (turnover) of the orientations of the radicals with respect to each other occurs in the original cages prior to combination. The basic problem in interpretation is one of consideration of a number of competitive fast processes—diffusion, recombination, disproportionation, and rotation. For clarity in presentation of an interpretation of the results, the D and L convention will be used in which *SS*-(−)-azobis-α-phenylethane is DD-(−) and *RR*-(−)-2, 3-diphenylbutane is DD-(−).[14] In Scheme II[18] are summarized the minimum number of processes needed to interpret the results. In this analysis, we assume that $k_{diff.}$, a rate constant for disappearance of a radical pair by the diffusion of one radical away from the other, is the same for all of the cages of Scheme II. The basis for this assumption is the essen-

(17) (a) Cage recombination, 28 ± 2%, plus cage disproportionation, 12/88 × 28. (b) Of the non-*meso* product, 6.9/20.45 = 33.5% results from cage reaction. Taking into account the preferential cage formation from *SS*-(−)-azo of non-*meso* dimer over *meso* dimer of 1.08 leads to a calculated value for total cage reaction of 32.5%. (c) S. Seltzer and E. J. Hamilton, *J. Am. Chem. Soc.*, 88, 3775 (1966). Approximations for the effect of deuterium on the relative intensities of fragmentation peaks exert some leverage on this number.

(18) The use of D and L here refers to the orientation of the radicals relative to the starting DD-azo compound, and *does not imply* nonplanar radicals; the radicals are presumed to be planar.

Scheme II



tial identity of the cage effect for both the non-*meso*- and *meso*-azo compounds (Table III). The constant, $k_{rot.}$ (Schemes I and II), is the rate constant for a 180° change in orientation (by out-of-plane rotation) of one α-phenylethyl radical relative to the other radical of the "caged" pair. We assume a single value of $k_{rotation}$ for interconversion between cages of Scheme II, based on the finding of equal yields of *meso* and non-*meso* dimers formed from statistically distributed α-phenylethyl radicals, and the yield and product data of Table III. The constants, $k_{comb.}$ and k_{disp}, are not the usual second-order termination rate constants but are first-order rate constants for the conversion of the radical pair cages of Scheme II to the combination and disproportionation products.

$k_{rot.}/k_{comb.}$. The ratio of principal interest in this study is the rate of rotation of one radical relative to its partner compared with the rate of combination of the two radicals. On the basis of the assumptions outlined above, one can derive expressions for the product composition in terms of the rate constants shown in Scheme II. A summary of calculated product distributions for various values of λ and a comparison with the observed distribution is given in Table VI. A value of λ = 4.1 affords a close fit between calculated and observed distributions. The terms in the denominator of eq 8 are all expressible in terms of $k_{comb.}$.

$$\lambda = k_{rot.}/(k_{comb.} + k_{disp} + k_{diff}) \quad (8)$$

$$\text{DD dimer} = \frac{(2\lambda + 1)^2 - 2\lambda^2}{(4\lambda + 1)(2\lambda + 1)} \quad (9)$$

$$\textit{meso} \text{ dimer} = \frac{2\lambda}{(4\lambda + 1)} \quad (10)$$

$$\text{LL dimer} = \frac{2\lambda^2}{(4\lambda + 1)(2\lambda + 1)} \quad (11)$$

$$\text{DD dimer} + \textit{meso} \text{ dimer} + \text{LL dimer} = 1 \quad (12)$$

$$k_{disp}/k_{comb.} = 12/88 \quad (13a)$$

$$\text{cage effect} = \frac{k_{comb.} + k_{disp}}{k_{comb.} + k_{disp} + k_{diff}} = 0.32 \quad (13b)$$

Table VI. Calculated Distribution of Diastereomeric 2,3-Diphenylbutanes from Cage Combination in Decomposition of DD-(−)-Azobis-α-phenylethane[a] as a Function of λ[b]

λ[b]	2,3-Diphenylbutanes, %[c] DD	DL (≡*meso*)	LL	Predicted optical purity of non-*meso*-2,3-diphenylbutane, %
Calculated				
0	100	0	0	
1	46.7	40.0	13.3	55.7
2	37.8	44.4	17.8	36.0
3	34.1	46.2	19.7	26.8
4	32.0	47.1	20.9	21.0
5	30.7	47.6	21.6	17.4
6	29.7	48.0	22.2	
7	29.2	48.3	22.5	
8	28.7	48.5	22.8	
9	28.3	48.7	23.0	
∞	25.0	50.0	25.0	
Observed				
(4.1)	31.3[d]	48.1[d]	20.6[d]	20.4[d]

[a] DD-(−)-Azo = ss-(−)-azo. [b] Equation 8. [c] Equations 9, 10, 11, and 12. [d] ±1%.

Table VII. Summary of Relative Rates[a] of Scheme II for λ = 4.1

Process	k_{rel}
$k_{comb.}$	1.0
k_{disp}	0.14
k_{diff}	2.4
$k_{rot.}$	15

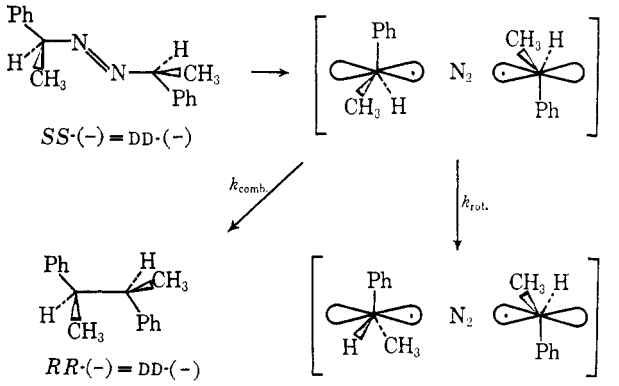
[a] Equations 8–13.

i.e.

$$\lambda = k_{rot.}/3.57k_{comb.} \quad (13c)$$

The principal comparison, $k_{rot.}/k_{comb.}$, is shown in Scheme III.

Scheme III



A second, mechanistically less specific, analysis of the product distribution may be made. Let us name the positions of the two α-phenylethyl radicals produced in the decomposition of DD-(−)-azobis-α-phenylethane site 1 and site 2. Let x be the extent of departure (expressed as a fraction) from a statistical distribution of the two radical configurations of interest, D and L.[18] The probability of a D configuration[18] at site 1 is 0.5 + x; the probability of L configuration[18] at site 1 is 0.5 − x; the probability of D configuration[18] at site 2 is 0.5 + x; and of L configuration[18] at site 2 is 0.5 − x.

$$\text{DD dimer} = (0.5 + x)^2 \quad (14)$$

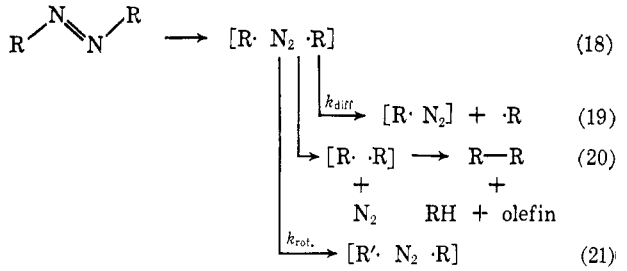
$$\textit{meso} \text{ dimer} = 2(0.5 + x)(0.5 - x) \quad (15)$$

$$\text{LL dimer} = (0.5 - x)^2 \quad (16)$$

$$\text{DD dimer} - \text{LL dimer} = 2x \quad (17)$$

For the cage combination associated with the decomposition of DD-(−)-azobis-α-phenylethane (Table V), $x = 0.054$. The predicted amount of *meso* product for this value of x is 49.4%, in reasonable agreement with the observed value of 48.1%. The probability of D configuration[18] at each site immediately after decomposition of DD-(−)-azo compound is 1.0. The results indicate a drop to 0.554 for the probability of D configuration[18] for each radical immediately before cage recombination. A drop to 0.50 would correspond to completely random orientation.

Is it reasonable for $k_{rot.}$ to exceed $k_{comb.}$ by the large amount implied in the above analyses? The most reasonable transition state for decomposition of acyclic azo compounds would appear to be one in which the C–N bonds are broken simultaneously[19] and in a way that places the resulting radicals on opposite sides of the nitrogen molecule (eq 18). The relationship between the ensuing processes may be viewed in the following way. All of the processes



(18)

(19)

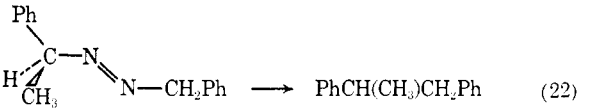
(20)

(21)

(k_{diff}, $k_{comb.}$, and $k_{rot.}$), are dependent on diffusive displacements. The process labeled here as k_{diff} refers to the creation of a "hole" near to R· and the diffusive displacement of R· away from the remaining R·N$_2$ (eq 19). The termination processes, $k_{comb.}$ and $k_{disp.}$, depend on the diffusive displacement of N_2 away from the R's and on the subsequent interaction between the R's (eq 20). The process of $k_{rot.}$ depends on the creation of a "hole" in the vicinity of R· large enough to permit rotation of the radical (eq 2 and Scheme III). Rotation of the α-phenylethyl radical appears to occur more readily than recombination in the experiments of this study. This may, in part, be due simply to a lower space requirement for this rotation than for diffusive displacement of the molecular nitrogen. Other factors being equal, one would expect $k_{rot.}$ to decrease as one replaces the benzylic hydrogen of the α-phenylethyl radical by a larger group.

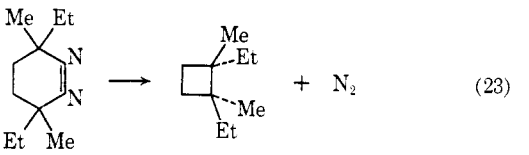
Data from dielectric relaxation studies provide a measure of the time required for rotation. Dielectric relaxation times for a number of aryl compounds (toluene, benzyl chloride, anisole, chlorobenzene) in benzene at 20° are in the range 10^{11}/sec.[20]

Relation to Other Cage Reactions. The principal finding of this study, $k_{rot.}/k_{comb.} \cong 15$, in benzene at 105° is in close accord with that of a parallel study on the optically active unsymmetrical azo compound, 1,1′-diphenyl-1-methylazomethane by Kopecky and Gillan[9] (eq 22), in which $k_{rot.}/k_{comb.} \cong 16$ in benzene at 110°.



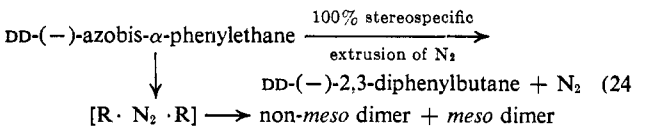
(22)

The use of an optically active ditertiary azo compound, 1,1′-diphenyl-1,2,1′,2′-tetramethylazopropane,[7a] has been attempted but unfortunately "cage recombination" in solution was too low to permit analysis of stereochemistry. Photolysis of the azo compound in frozen benzene at −190° showed high preference for formation of non-*meso* product from non-*meso* reactant,[7a] *i.e.*, in that experiment diffusion of nitrogen took place more readily than rotation of the tertiary radicals. A ditertiary cyclic system, 3,6-dimethyl-3,6-diethyl-1,2-pyridazine, has afforded the interesting finding of high preference for conversion of non-*meso* reactant to non-*meso* product, presumably of over-all retention of configuration (eq 23).[21] Decomposition of pyrazolines appears to take a different course, and has been shown in some cases to involve a small net inversion of configuration.[22]



(23)

With the acyclic azo compound of the present study, the possibility of stereospecific extrusion of nitrogen (eq 24) has been considered and dismissed. The maximum amount of DD dimer formable in this way (Table V) is 10.7%, leaving a balance of 41.2% *dl* dimer and 48.1% *meso* dimer to be formed by other means. Such a predominance of *meso*, in excess of even the statistical finding, seems unreasonable. Basically, the close accord between the observed product composition and that calculated along straightforward statistical considerations (Scheme II and Table IV) leaves little room for alternate schemes which employ combinations of stereospecific extrusion of N_2 plus radical recombination paths.



(24)

The relation between stereochemistry of radical recombination and the relative locations of the radicals immediately after bond cleavage is of special interest. As indicated in eq 12, the decomposition of acyclic azo compounds in all likelihood generates radicals on opposite sides of the N_2. Diazenes[13b,23] represent a possible route to a different orientation of the same fragments. If diazene decomposition proceeded by homolysis, these

(19) See S. Seltzer and S. G. Mylonakis, *J. Am. Chem. Soc.*, **89**, 6584 (1967), and references cited therein.

(20) C. P. Smyth, Special Publication No. 20, The Chemical Society, London, 1965, pp 1–14.

(21) P. D. Bartlett and N. A. Porter, *J. Am. Chem. Soc.*, **90**, 5317 (1968).

(22) See R. Moore, A. Mishra, and R. J. Crawford, *Can. J. Chem.*, **46**, 3305 (1968), and E. L. Allred, J. C. Hinshaw, and A. L. Johnson, *J. Am. Chem. Soc.*, **91**, 3382 (1969), and references cited in these papers.

(23) (a) C. G. Overberger, M. Valentine, and J. P. Anselme, *J. Am. Chem. Soc.*, **91**, 687 (1969); (b) C. G. Overberger and N. P. Marullo, *ibid.*, **83**, 1378 (1961); (c) D. M. Lemal and S. D. McGregor, *ibid.*, **88**, 1335 (1966).

radicals, now generated close together and with the N_2 off to one side, might be expected to form coupling products with higher stereospecificity than observed with acyclic azo compounds.[24]

Stereospecificity in decomposition of diacyl peroxides, $(RCOO)_2$, raises a problem both with regard to ester, RCOOR, and dimer, RR.[15b,25] Previous studies have established that the ester formed from *sec*-diacyl peroxides arises from intramolecular rearrangement of peroxide to carboxy inversion product,[25] followed by conversion to ester. The hydrocarbon dimer, RR, has been proven to arise from peroxide by a first-order process[26] but its mechanism of formation remains unknown. The isolation of non-*meso*-2,3-diphenylbutane of 13% retention of configuration from the action of Na_2O_2 on $C_6H_5CH(CH_3)COCl$ at $-40°$ [27] is of interest in this regard but the conditions of its formation differ too much from the azo decomposition to warrant further discussion.

In summary, the present study provides evidence for some stereospecificity in the conversion of an azo compound to dimer *via* a process which, with high probability, has proceeded through a radical pair separated by a nitrogen molecule. By implication, radical pairs generated closer together might recombine with higher stereospecificity. This has important implications for rearrangement studies in that a finding of high stereospecificity should not be taken as evidence against a radical pair pathway. Generation of radical pairs in close proximity may also take place by bimolecular reactions between nonradical species. Here too, radical pairs, lacking an intervening molecule (such as nitrogen in azo decompositions), might recombine with high stereospecificity. The oxidation of tertiary hydrocarbons by chromic acid has been suggested to proceed in this way.[28] The recently reported conversion of alkanes to alcohols by ozone[29] with complete retention of configuration also may be an example of this type of reaction.

Studies of the effect of solvent, temperature, pressure, etc. on stereochemistry and yield in cage recombination reactions hold promise of providing intimate details on the behavior of molecules in a liquid medium.[7] At present it is clear that $k_{comb.}$ is slowed by appreciable bulk at the radical sites [*e.g.*, $C_6H_5C(CH_3)$(isopropyl) from the corresponding azo compound][7a] presumably quite apart from the problem of diffusion of the nitrogen molecule, but the effect of reaction variables on $k_{rot.}$, $k_{comb.}$, and k_{diff} is harder to predict.

Relation of the Results of this Study to the Geometry of Radicals. Several studies have appeared in which optically active products have been derived from cage reactions and in which the conclusion has been drawn that the optical results constitute evidence for nonplanar radical intermediates.[4d,e] Perhaps when more becomes known of the ease of rotation of various radicals in different media it may be possible to relate such results to radical geometry. But, at present it is clear that rotational considerations alone can account for the stereochemistry observed, and the findings of stereospecificity in cage reactions reported to date do not provide an adequate basis for conclusions on radical geometry.

Experimental Section

Gas–Liquid Partition Chromatography. Column A is a 7 ft 0.25 in. diameter aluminum tube packed with 20% SE-30 on 80/100 mesh Chromosorb P diatomite; column B, 15 ft, 0.375 in. diameter aluminum tube packed with 15% SE-30 on 80/100 mesh Chromosorb P diatomite; column C, fitted to an Aerograph Model 600 flame instrument using a 15 ft, 0.125 in. diameter aluminum tube packed with 15% SE-30 on 80/100 mesh Chromosorb P with a 250° injector temperature and a nitrogen back pressure of 50 psi; column D, 15 ft, 0.250 in. diameter aluminum tube packed with 15% Carbowax 20M on 80/100 mesh Chromosorb W diatomite; column E, fitted to an Aerograph Model 600 flame instrument using a 15 ft, 0.125 in. diameter aluminum tube packed with 15% Carbowax 20M on 80/100 mesh Chromosorb W diatomite with a 250° injector temperature and a nitrogen back pressure of 50 psi. All identifications of vpc components except where noted were made by the identity with an authentic sample of both the retention time and ir spectrum of a collected sample. All quantitative analyses were done by using an internal standard. The benzene used for the decompositions was freshly distilled from a mixture of benzophenone and sodium in a mole ratio of 1:1. The test tubes were thoroughly washed with distilled water and dried in a vacuum oven.

***S*-(−)-α-Phenylethylamine.** The resolution procedure of Theilacker[30] was used giving levorotatory amine have $[\alpha]^{22}D$ −40.1° (neat) assuming d^{22}_4 0.950 (lit.[1] $[\alpha]^{22}D$ −40.3°).

***SS*-(−)-N,N′-α-Phenylethylsulfuric Acid Diamide.** *S*-(−)-α-Phenylethylamine (75.1 g, 0.621 mole, $[\alpha]^{22}D$ −40.1°) was added to 300 ml of hexane under a nitrogen atmosphere. The solution was cooled under stirring to −5° and sulfuryl chloride (21.6 g, 0.160 mole) in 50 ml of hexane added dropwise. After the mixture was refluxed for 2 hr and stirred for 4 hr, it was quenched in water, acidified with hydrochloric acid, and extracted six times with ethyl ether. After drying ($MgSO_4$) and removing the ether, the initial solid residue was twice recrystallized from ethanol–water yielding 30.9 g (63.5% based on sulfuryl chloride) of a white solid: mp 99–100°; $\alpha^{25}D$ −75.6° (66.4 mg/2 ml of C_2H_5OH); ir (CCl_4) 3260 cm^{-1} (NH), 1325, and 1125 cm^{-1} (SO_2); uv max (CH_3OH) 258 mμ (ε = 358); nmr ($DCCl_3$) δ 7.23 (s, 10, aromatic protons), 4.95 (d, 2, *J* = 8.0 Hz, CHN*H*S), 4.43 (m, 2, *J* = 8.0 Hz, C*H*NH) and 1.43 ppm (d, 6, *J* = 8.0 Hz, C*H*$_3$CH); mass spectrum (80 eV) *m/e* (relative intensity) 304 (1), 289 (22.8), 167 (49.7), 105 (196.5), 77 (96.4) (*Anal.* Calcd for $C_{16}H_{20}N_2O_2S$: C, 63.13; H, 6.62; N, 9.20; S, 10.53. Found: C, 63.41; H, 6.70; N, 9.14; S, 10.44).

***SS*-(−)-Azobis-α-phenylethane.** Using the procedure of Ohme and Schmitz[31] *SS*-(−)-N,N′-α-phenylethylsulfuric acid diamide (12.52 g, 0.0412 mole, $[\alpha]^{25}D$ −75.6°) was added to 250 ml of a 1 *M* sodium hydroxide solution. The mixture was purged with nitrogen for 2 hr under stirring. Sodium hypochlorite (60 ml, 1.5 *M*) was added dropwise over a period of 30 min, the mixture stirred for 2 hr at 60°, and then stirred overnight at 25°. The crude product was extracted three times with pentane, concentrated, and chromatographed on a column of 150 g of neutral alumina (activity II) shielded from the light using pentane as the solvent yielding 4.62 g (47.1%) of a pale yellow liquid. Rechromatography of 300 mg of this material on a similar column separated 2.5 mg of 2,3-diphenylbutane as a small fraction prior to the main azo fraction. Subsequent chromatography showed the product possessed less than 0.1% of the diphenylbutanes. The recovered product had $[\alpha]^{25}D$ −304.9° (35.8 mg/2 ml of CCl_4): ir (CCl_4) 2970 (CH), 1600 and 590 cm^{-1} (aromatic); uv max (CH_3OH) 354 mμ (ε 56); nmr ($CDCl_3$) δ 7.46 (m, 10, aromatic protons), 4.76 (quartet, 2, *J* = 7.0 Hz, C*H*CH$_3$), and 1.56 ppm (d, 6, *J* = 7.0 Hz, CHC*H*$_3$) (*Anal.* Calcd for $C_{16}H_{18}N_2$: C, 80.63; H, 7.61; N, 11.76. Found: C, 80.88; H, 7.82; N, 11.70).

(24) Analysis of the product data for the oxidation by mercuric oxide of *SS*-(−)-$[C_6H_5CH(CH_3)]_2NNH_2$ in ethanol at 60°, eq 2, (ref 13b) by eq 8–11 affords a value of λ (Table VI) of 1.5–2. For a cage effect of 0.5–0.75, $k_{rot.}/k_{comb.} \cong 2.5$–4. However, the lack of quantitative data on DD, LL, and *meso* product composition in that reaction, and the difference in reaction conditions from those of this study, render the comparisons of $k_{rot.}/k_{comb.}$ no more than suggestive.

(25) See F. D. Greene, H. P. Stein, C-C. Chu, and F. M. Vane, *J. Am. Chem. Soc.*, **86**, 2080 (1964), and references cited therein.

(26) D. F. DeTar and C. Weis, *ibid.*, **79**, 3041 (1957).

(27) This experiment, originally reported in ref 15b, has been repeated (ref 1d) and is reported in the Experimental Section of this paper.

(28) K. B. Wiberg and G. Foster, *J. Am. Chem. Soc.*, **83**, 423 (1961).

(29) T. M. Hellman and G. A. Hamilton, 157 National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, Abstracts, ORGN-071.

(30) W. Theilacker and H.-G. Winkler, *Chem. Ber.*, **87**, 690 (1954).

(31) R. Ohme and E. Schmitz, *Angew. Chem.*, **77**, 429 (1965).

meso-**Azobis-α-phenylethane.** The procedure of Cohen[32] was followed yielding a crystalline pale-yellow solid: mp 71–72° (lit.[32] mp 72–73°); uv max(CH_3OH) 355 mμ (ε 51) (lit.[3] 355 mμ (ε 48.6)).

Hydrogenolysis of *SS*-(−)-Azobis-α-phenylethane. *SS*-(−)-Azobis-α-phenylethane (0.625 g, 2.62 mmoles, $[\alpha]^{25}D$ −304.9°) in 5 ml of ethanol was added to a solution containing 15 ml of ethanol, 15 ml of water, and 5 ml of glacial acetic acid. The solution was heated to 50° and zinc dust (7.30 g, 0.112 mole) added slowly over a period of 1 hr. The mixture was stirred at such a rate that globules of zinc about 0.25 in. in diameter formed. The rate of stirring was critical; higher rates appeared to slow the reaction even at higher temperatures. The mixture was then stirred for 2 hr at 50°, neutralized with sodium hydroxide, and the product quickly extracted with ethyl ether. After drying ($MgSO_4$), vpc (column A, 125°) showed 0.253 g (40%) of α-phenylethylamine present. The amine was collected by vpc (column B, 135°) having $[\alpha]^{24.3}_{546}$ −33.4° (64.7 mg/1 ml of C_2H_5OH). *S*-(−)-α-Phenylethylamine having $[\alpha]^{22}D$ −40.1° (neat) gave $[\alpha]^{24.3}_{546}$ = −36.2° (65.5 mg/1 ml of C_2H_5OH). S-(−)-α-Phenylethylamine (0.330 g) exposed to these same hydrogenolysis conditions and isolated by identical vpc procedures gave $[\alpha]^{24.2}_{436}$ −56.9° (29.4 mg/2 ml of C_2H_5OH). *S*-(−)-α-Phenylethylamine having $[\alpha]^{22}D$ −40.1° (neat) gave $[\alpha]^{24.2}_{436}$ = −60.1° (30.0 mg/2 ml of C_2H_5OH).

Decomposition of Di-*t*-butyl Peroxide in the Presence of Ethylbenzene. Ethylbenzene (1.06 g, 10 mmoles) and di-*t*-butyl peroxide (0.25 g, 1.73 mmoles) were added to 10 ml of benzene, sealed in an ampoule after degassing three times to 0.01 mm by alternate freezing with liquid nitrogen and thawing, and decomposed for 10 days at 105°. The ampoule was then opened, the benzene concentrated and the ratio of the non-*meso*/*meso*-2,3-diphenylbutane found to be 1.00 ± 0.03 by vpc (column C, 170°). *meso*-2,3-Diphenylbutane was found to be stable with respect to formation of non-*meso*-2,3-diphenylbutane when exposed to di-*t*-butyl peroxide under these conditions.

Decomposition of di-*t*-butyl diperoxyoxalate[33] (0.43 g) in ethylbenzene at 30° for 2 days and analysis by glpc indicated a non-*meso*/*meso*-2,3-diphenylbutane ratio of 1.00.

Demonstration of the Absence of Possible By-Products in the Dimerization of α-Phenylethyl Radicals. Analysis of the reaction mixtures by glpc gave only three peaks, corresponding to *meso*- and non-*meso*-2,3-diphenylbutane and a small amount of an unknown: compound (retention time relative to dibenzyl ≡ 1.00), *dl*-2,3-diphenylbutane (1.31), *meso*-2,3-diphenylbutane (1.45), unknown (1.57), 1-(4-ethylphenyl)-1-phenylethane (1.78), 1,3-diphenylbutane (1.80), 4,4′-diethylbiphenyl(2.93).

2,3-Diphenylbutanes from the Reaction of (+)-2-Phenylpropionyl Chloride with Alkaline Hydrogen Peroxide.[15b] A sample of the acid chloride (prepared from 5.88 g of hydrotropic acid, $[\alpha]^{27}D$ +98.3°) and a solution of 7 g of NaOH and 7.5 ml of 30% H_2O_2 in 50 ml of water was stirred at 0° for 2 days. Extraction with ether, chromatography on alumina, and analysis of the hydrocarbon fraction by glpc and optical rotation indicated the composition of the 2,3-diphenylbutanes to be *meso*, 50 ± 1%; *RR*-(−), 28.3%; *SS*-(+), 21.7%.

N-*t*-Butyl-α-phenylethylamine was prepared by a method similar to that used by Novelli.[34] Formic acid (7.6 g, 0.166 mole) was added cautiously to *t*-butylamine (12.1 g, 0.166 mole) at −5°. Water was removed by heating over a 30-min period. The solution was cooled to 80° and acetophenone (5.0 g, 0.0416 mole) added. After refluxing the material for 1 hr, all the material was distilled slowly into 250 ml of aqueous 1 *M* HCl. Acetophenone was removed by extraction with ethyl ether. The aqueous layer was neutralized (NH_4OH), the amine extracted with ether, and the ether layer dried ($MgSO_4$). The product was collected by glpc (column A, 135°): ir (CCl_4) 3320 (NH, very weak), 2950, 1600 and 597 cm^{-1}; nmr (CCl_4) δ = 7.10 (m, 5, aromatic), 3.84 (q, 1, *J* = 7 Hz, C*H*CH_3), 1.22 (d, 3, *J* = 7 Hz, CHC*H*$_3$), and 0.95 ppm (s, 9, C*H*$_3$); mass spectrum (80 eV) *m/e* (relative intensity) 177 (44.5), 162 (149), 106 (124), 105 (756), 77 (124), 58 (205) (*Anal.* Calcd for $C_{12}H_{19}N$: C, 81.30; H, 10.80; N, 7.90. Found: C, 81.34; H, 11.03; N, 7.80).

Non-*meso*-2,3-diphenylbutane. *trans*-α,α′-Dimethylstilbene[35a] was hydrogenated at 1 atm with a 5% palladium on carbon catalyst[35b] in 20 ml of ethyl acetate yielding 761 mg (75%) of a clear liquid after distillation through a short-path microstill, pot temperature 65° (1 mm). Vpc (column C, 170°) indicated 2% *meso*-2,3-diphenylbutane was present as an impurity.

meso-**2,3-Diphenylbutane.** This material was prepared by the action of magnesium on α-phenylethyl bromide.[36] The *meso*-2,3-diphenylbutane was isolated by crystallization yielding a white solid, mp 125–128° (lit.[37] mp 126.4–127.0°).

Equilibration of Non-*meso*- and *meso*-2,3-Diphenylbutane. Glass tubes containing 100 mg of the *dl* isomer or 100 mg of the *meso* isomer, 0.3 g-atom of potassium metal, and 1 ml of di-*n*-butylamine (dried over potassium) were degassed and sealed under vacuum.[11] After 21 days in constant-temperature baths at 80.1 and 126.5° or 34 days at 49.60°, the tubes were opened and the solutions were analyzed by gas chromatography. The results are shown in Table II.

Decomposition of *SS*-(−)-Azobis-α-phenylethane. *SS*-(−)-Azobis-α-phenylethane (0.1374 g, 0.578 mmole, $[\alpha]^{25}D$ −304.9°) was diluted to 10 ml with benzene. This solution was placed in an ampoule, degassed three times to 0.01 mm by alternate freezing with liquid nitrogen and thawing, sealed, and placed in a constant-temperature bath at 105° for 36 hr. The ampoule was then opened and the benzene removed under reduced pressure. The yield of *meso*- and non-*meso*-2,3-diphenylbutane was found by vpc (column C, 170°) to be 88 ± 2% averaged over four decompositions where the non-*meso*/*meso* ratio was 1.01 ± 0.03. The non-*meso* retention time was 62 min and the *meso*, 70 min. The non-*meso* product from four such decompositions was collected by vpc (column B, 160°, ten injections) and combined to give sample A. Sample A was found to still possess a 3.3 ± 1% *meso* impurity by further vpc (columns C and E, 170°). Adjusting for the *meso* content, sample A gave $[\alpha]^{25}D$ −6.96° (86.3 mg/2 ml of C_2H_5OH, α_{obsd} = −0.301°). The ethanol from sample A was removed and the residue chromatographed with pentane on 150 g of neutral alumina (activity I). The 2,3-diphenylbutane fraction was recollected by vpc (column D, 160°, six injections) to give sample B, which possessed $[\alpha]^{25}D$ −6.69° (26.0 mg/2 ml of C_2H_5OH, α_{obsd} = −0.087°). Further vpc (columns C and E, 170°) work on sample B indicated no impurities except for less than 0.2% of the *meso* isomer. Sample B had mass spectral, infrared, and vpc properties identical with vpc-collected (column D, 160°) non-*meso*-2,3-diphenylbutane prepared by the hydrogenation of *trans*-α,α′-dimethylstilbene.

Scavengers. The scavengers employed to capture noncage radicals were thiophenol and 2-methyl-2-nitrosopropane. 2-Methyl-2-nitrosopropane was synthesized from *t*-butylhydroxylamine by oxidation with 1 equiv of bromine in aqueous base.[38] The product was recrystallized from pentane yielding a white solid, dec pt 73–75° (lit.[38] dec pt 83–84°).

Conditions for maximum scavenging efficiency were achieved with both scavengers, since increasing the concentration of scavenger above the concentrations used for the decompositions did not affect the yield of coupled product, 2,3-diphenylbutane.

When used as scavenger, 2-methyl-2-nitrosopropane did not attack *meso*-azobis-α-phenylethane, since equal amounts of unreacted azo compound were recovered after 1.5 half-lives decomposition with and without scavenger. However, thiophenol did attack *meso*-azobis-α-phenylethane as was indicated by a ~10% yield of acetophenone azine. With thiophenol as scavenger the other products recovered and identified by comparison with authentic samples were ethylbenzene (~57%), phenyl disulfide (~39%), and α-phenylethyl phenyl sulfide (~1%).

Decompositions with thiophenol as scavenger were run through at least 10 half-lives. Decompositions with 2-methyl-2-nitrosopropane as scavenger were run through 1.5 half-lives. Increasing the time for decomposition to 14 hr did not increase the per cent yield of 2,3-diphenylbutane after adjusting for recovered azo compound.

Decomposition of *SS*-(−)-Azobis-α-phenylethane with 2-Methyl-2-nitrosopropane as Scavenger. *SS*-(−)-Azobis-α-phenylethane (0.5024 g, 2.21 mmoles, $[\alpha]^{25}D$ −304.9°) was added to 15 ml of benzene. 2-Methyl-2-nitrosopropane (2.006 g, 23.0 mmoles) was added and the solution diluted to exactly 20 ml. The solution was then divided in half, placed in two ampoules, degassed, sealed, and placed in a constant-temperature bath at 105° for 3 hr. The am-

(32) S. G. Cohen, S. J. Groszos, and D. B. Sparrow, *J. Am. Chem. Soc.*, 72, 3947 (1950).
(33) P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *ibid.*, 82, 1762 (1960).
(34) A. Novelli, *ibid.*, 61, 520 (1939).
(35) (a) W. R. Brasen, S. W. Kantor, P. S. Skell, and C. R. Hauser, *ibid.*, 79, 397 (1957); (b) R. Mozingo, "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1955, p 686.
(36) D. A. Shirley, "Preparation of Organic Intermediates," John Wiley & Sons, Inc., New York, N. Y., 1951, p 76.
(37) K. T. Serijan and P. H. Wise, *J. Am. Chem. Soc.*, 74, 365 (1952).
(38) W. D. Emmons, *ibid.*, 79, 6522 (1957).

poules were then opened and most of the solvent and scavenger were removed under reduced pressure. The remaining residue was taken up in pentane, chromatographed with pentane on a column (shielded from light) of 150 g of neutral alumina (activity II), and separated into the 2,3-diphenylbutanes and unreacted azo fractions. The 2,3-diphenylbutanes preceded the azo portion. After adjusting for the recovered azo material, the yield of non-*meso* and *meso*-2,3-diphenylbutane with added bibenzyl as standard was found by vpc (column C, 170°) to be 28 ± 2% averaged over six decompositions where the ratio of non-*meso* to *meso* was 1.05 ± 0.03. The recovered azo fractions from six runs were all combined and rechromatographed as before to give material which had $[\alpha]^{25}D$ −299.2° (35.8 mg/2 ml of CCl_4). The non-*meso*-2,3-diphenylbutane from the six runs was collected by vpc (column B, 160°, fifteen injections) and distilled in a short-path, microstill at 1 mm and 60° pot temperature to give sample C. Sample C was found to possess a 4.8 ± 1% *meso* impurity by further vpc (column C, 170°). Adjusting for this *meso* content, sample C gave $[\alpha]^{25}D$ −20.0° (79.4 mg/2 ml of C_2H_5OH, α_{obsd} = −0.794°). Sample C was then recollected by vpc (column D, 160°, ten injections) giving sample D which had $[\alpha]^{25}D$ −20.1° (38.8 mg/2 ml of C_2H_5OH, α_{obsd} = −0.391°). The average value is $[\alpha]^{25}D$ −20.1 ± 0.1°. The error is assigned as the discrepancy between the two rotational values obtained. Further vpc (columns C and E, 170°) indicated that sample D possessed no impurities except less than 0.1% of the *meso* isomer. Sample D had mass spectral, infrared and vpc properties identical with vpc-collected (column D, 160°) non-*meso*-2,3-diphenylbutane prepared by the hydrogenation of *trans*-α-α′-dimethylstilbene.

Glpc analysis of the original product solution indicated the presence of two additional compounds in approximately 5% yield: acetophenone and N-*t*-butyl-α-phenylethylamine, identical in retention time and ir with authentic samples. It is thought that these products are derived from reaction of α-phenylethyl radicals with the scavenger nitroso-*t*-butane.

Decomposition of *SS*-(−)-Azobis-α-phenylethane with Thiophenol as Scavenger. *SS*-(−)-Azobis-α-phenylethane (2.396 g, 0.0101 mole, $[\alpha]^{25}D$ −301.7°) was combined with thiophenol (10.0 g, 0.0909 mole) and diluted to 150 ml with benzene. This solution was transferred to 15 ampoules in 10-ml aliquots, degassed, and sealed as before. The ampoules were placed in an oil bath maintained at 105° for 36 hr. The ampoules were then opened, and their contents washed with aqueous potassium hydroxide. After drying ($MgSO_4$), the benzene was removed under reduced pressure. The 2,3-diphenylbutanes were collected in ten injections using preparative vpc (column B, 190°) with no attempt at separation into the non-*meso* and *meso* isomers. The collected 2,3-diphenylbutanes were further purified by column chromatography on 150 g of neutral alumina (activity II). The non-*meso* product was partially extracted from the *meso* with absolute ethanol, since the *meso* solid is fairly insoluble in ethanol. The extraction yielded 0.0770 g of material which when diluted to 2 ml with absolute ethanol gave α^{25}_{obsd} −0.591°. Subsequent vpc data (column C, 170°), showed that this material still possessed 24.7 ± 2% *meso*-2,3-diphenylbutane; this leads to a value of $[\alpha]^{25}D$ −20.4 ± 0.6° for the non-*meso* isomer. The error is computed from the error in the *meso* measurements. Further vpc analysis (columns D and E, 170°) showed no peaks other than the *meso*- and non-*meso*-2,3-diphenylbutanes. The material used for the rotation determination was repassed through the preparative vpc column to obtain sample E. Sample E had identical mass spectral, infrared, and vpc properties with vpc collected non-*meso*-2,3-diphenylbutane prepared by the hydrogenation of *trans*-α,α′-dimethylstilbene.

Acetophenone-d_3. Into a dry 500-ml flask equipped with a $CaCl_2$ drying tube atop a reflux condenser was placed deuterium oxide (60.0 g, 3.0 moles), acetophenone (34.4 g, 0.29 mole), and 200 ml of dimethoxyethane distilled from sodium. Na_2CO_3 (0.4 g) was added and the mixture refluxed for 24 hr. After the addition of NaCl (100 g), the deuterium oxide layer was separated and the dimethoxyethane layer dried ($MgSO_4$). The procedure was repeated twice more on the dimethoxyethane filtrate obtained after removal of the $MgSO_4$. Then, after final drying of the dimethoxyethane, the solvent was removed and the residue distilled to give 26.1 g (74.1%) of product: bp 80° (9 mm); mass spectrum (80 eV) *m/e* (relative intensity) 123 (32.8), 122 (1.0), 121 (0.1); the mass spectrum of undeuterated acetophenone showed an *m* − 1 peak of 1% of the *m* peak.

***meso*-2,3-Diphenylbutane-d_6.** This material was prepared by reducing acetophenone-d_3 to the alcohol-d_3 with $LiAlH_4$, converting the alcohol-d_3 to the corresponding bromide-d_3, with gaseous hydrogen bromide in pentane and coupling with magnesium in ethyl ether. After removal of the ether, the crystals of the *meso* isomer were washed with cold hexane and recrystallized once from ethanol–water and once from ethanol giving 1.39 g (22% based upon the total amount of 2,3-diphenylbutane expected) of a white solid: mp 124–124.5°; vpc (column C, 170°) showed no non-*meso*-2,3-diphenylbutane impurity; nmr (CS_2) showed no CH for methyl absorption; ir (CS_2) 2200 and 2050 cm^{-1} characteristic of the deuterated compound; mass spectrum (80 eV) *m/e* (relative intensity) 216 (92), 215 (7), 210 (0.1).

Ethylbenzene-β-d_3. This material was prepared by the reaction of $LiAlH_4$ with α-phenylethyl-d_3 bromide in ethyl ether. The reaction was incomplete after 48 hr stirring at 26° and more drastic conditions (THF with reflux) led to the formation of the coupling product, 2,3-diphenylbutane, as the major product. The desired product from the incomplete reaction in ether was isolated as needed by vpc (column B, 140°) yielding a clear liquid: ir (CCl_4) 2200 and 2075 cm^{-1} characteristic of the deuterium label.

Thiophenol-*d* was prepared according to the procedure of Earnshaw.[39] Nmr showed the product to be 95% deuterated.

Decomposition of *meso*-Azobis-α-phenylethane with Thiophenol as Scavenger in the Presence of Added *meso*-2,3-Diphenylbutane-d_6. *meso*-Azobis-α-phenylethane (0.196 g, 0.824 mmole), thiophenol (1.059 g, 9.62 mmoles), and *meso*-2,3-diphenylbutane-d_6 (0.103 g, 0.478 mmole, 92% d_6) were placed in 10 ml of benzene. The solution was degassed as before, sealed in an ampoule, and decomposed for 36 hr at 105°. The ampoule was opened, the benzene solution washed with aqueous sodium hydroxide, and dried ($MgSO_4$). The non-*meso*-2,3-diphenylbutane in the solution was collected by vpc (column B, 160°) first as a shoulder due to the large excess of deuterated label and then reinjected to give the pure non-*meso* material. Mass spectral analysis indicated 0.8% conversion of the added *meso*-2,3-diphenylbutane-d_6 to the non-*meso* isomer.

(39) D. G. Earnshaw, G. L. Cook, and G. U. Dineen, *J. Phys. Chem.*, **68**, 296 (1964).