

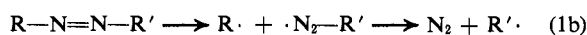
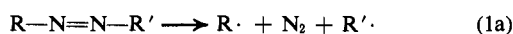
# On Internal Return of Caged Geminate Radicals Produced from Optically Active Methylazo- $\alpha$ -phenylethane<sup>1</sup>

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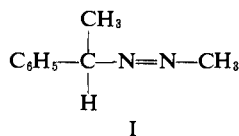
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**Abstract:** Methylazo- $\alpha$ -phenylethane (I), previously shown to undergo thermal decomposition by a stepwise mechanism, has been prepared optically active. The rate of loss of optical activity *vs.* the rate of nitrogen appearance indicates that no more than one out of 30 geminate pairs of caged  $\alpha$ -phenylethyl and azomethyl radicals return to I with racemization in solvent hexadecane and one out of 16 return in Nujol at 162°.

Previous studies reported from this laboratory have been concerned with the relative timing of the two carbon-nitrogen bond ruptures during the thermal decomposition of aralkylazo compounds (eq 1).<sup>2</sup>

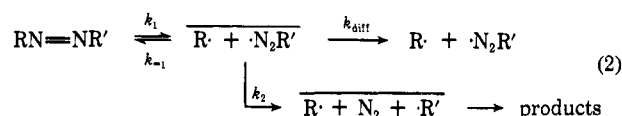


Examination of the kinetic isotope effects observed during thermal decomposition indicates a spectrum of mechanisms—from concerted equal bond rupture to stepwise scission of both bonds. Within a series of related azo compounds the choice of a particular mechanism appears to be determined by the relative ability of R and R' to delocalize a free spin. When R = R' =  $\alpha$ -phenylethyl a concerted mechanism (eq 1a) obtains. When R =  $\alpha$ -phenylethyl and R' = methyl as in I,



however, the compound decomposes by a stepwise mechanism (eq 1b) as indicated by secondary  $\alpha$ -deuterium, <sup>13</sup>C,<sup>2a</sup> and <sup>15</sup>N<sup>2d</sup> kinetic isotope effects.

Recently, other tests for establishing mechanism in thermal decompositions have been proposed. The observation of a decreased rate of gas evolution with increasing solvent viscosity in thermal decomposition studies has been advanced as a criterion for choosing between a stepwise or simultaneous concerted rupture of two or more reactive bonds in azo or peroxide molecules.<sup>3</sup> For example, in the case of azo compounds undergoing stepwise rupture,  $k_{\text{diff}}$  (eq 2) is expected to decrease with increasing solvent viscosity and thereby to provide a longer lifetime for the initially formed caged geminate radicals and greater probability for



return ( $k_{-1}$ ) to azo compound. Return has been suggested to be less probable from three fragments arising from concerted rupture of two bonds (eq 1a).<sup>3a</sup> The demonstration of <sup>18</sup>O scrambling during partial decomposition of acetyl peroxide has provided direct evidence of return of geminate caged radicals from decomposition of peroxides<sup>3d,e,4</sup> but such evidence is lacking in the case of azo compounds. Since there is independent evidence that suggests I decomposes by a stepwise mechanism we have chosen to look for return by a different method. This report describes the synthesis of (–)-methylazo- $\alpha$ -phenylethane ((–)-I) and the measurements of its rate of loss of optical activity compared to its rate of loss of nitrogen under the same conditions.

While this work was in progress two reports appeared on related cage effects.<sup>5</sup> Both of these studies have sought to measure the relative rates of coupling, disproportionation, rotation, and diffusive escape of caged geminate hydrocarbon radicals derived from the simultaneous rupture of the two carbon-nitrogen bonds of azo compounds. While these studies add considerably to our knowledge of cage processes of alkyl radicals they emphasize our lack of knowledge about the relative rates of reactions that caged hydrocarbon and azo radicals, formed by one bond scission, undergo.

## Experimental Section

Hexamethylbenzene, diphenylmethane, hexadecane (Eastman), and Nujol (Plough, Inc) were all used without further purification.

(–)-Methylazo- $\alpha$ -phenylethane. *N*-Methyl-*N'*- $\alpha$ -phenylethylhydrazine (163.8 g, 1.090 mol) was prepared by the method described previously<sup>2a</sup> and was dissolved in 150 ml of 95% ethanol. This solution was added to a solution of 180 g (1.20 mol) of (+)-tartaric acid (Eastman Co., mp 171–173°) in 400 ml of 95% ethanol. While the solution was stirred efficiently under a nitrogen atmosphere to prevent oxidation, 550 ml of ether was added gradually to avoid immediate precipitation of the salt. The solution was left at room temperature whereupon crystallization occurred and then refrigerated overnight in a nitrogen atmosphere. The solution was filtered and the precipitate dried: yield, 278.6 g, mp 90.5–96°. Seven

(1) (a) Research performed under the auspices of the U. S. Atomic Energy Commission. (b) On leave from Democritos, Greek Atomic Energy Commission.

(2) (a) S. Seltzer and F. T. Dunne, *J. Amer. Chem. Soc.*, **87**, 2628 (1965); (b) S. Seltzer, *ibid.*, **83**, 2625 (1961); (c) S. Seltzer, *ibid.*, **85**, 14 (1963); (d) S. Seltzer and S. G. Mylonakis, *ibid.*, **89**, 6584 (1967); (e) S. E. Scheppele and S. Seltzer, *ibid.*, **90**, 358 (1968); (f) S. G. Mylonakis and S. Seltzer, *ibid.*, **90**, 5487 (1968).

(3) (a) W. A. Pryor and K. Smith, *ibid.*, **92**, 5403 (1970); **89**, 1741 (1967); see also: (b) H. Kiefer and T. G. Traylor, *ibid.*, **89**, 6667 (1967); (c) R. C. Neuman, Jr., and R. J. Bussey, *ibid.*, **92**, 2440 (1970); (d) J. C. Martin and J. H. Hargis, *ibid.*, **91**, 5399 (1969); (e) J. W. Taylor and J. C. Martin, *ibid.*, **89**, 6904 (1967); (f) T. Koenig, J. Huntington, and R. Cruthoff, *ibid.*, **92**, 5413 (1970).

(4) There is disagreement on the exact amount of return from caged acetoxy radicals. See M. J. Goldstein and H. A. Judson, *ibid.*, **92**, 4119 (1970).

(5) (a) K. R. Kopecky and T. Gillan, *Can. J. Chem.*, **47**, 2371 (1969); (b) F. D. Greene, M. A. Berwick, and J. C. Stowell, *J. Amer. Chem. Soc.*, **92**, 867 (1970).

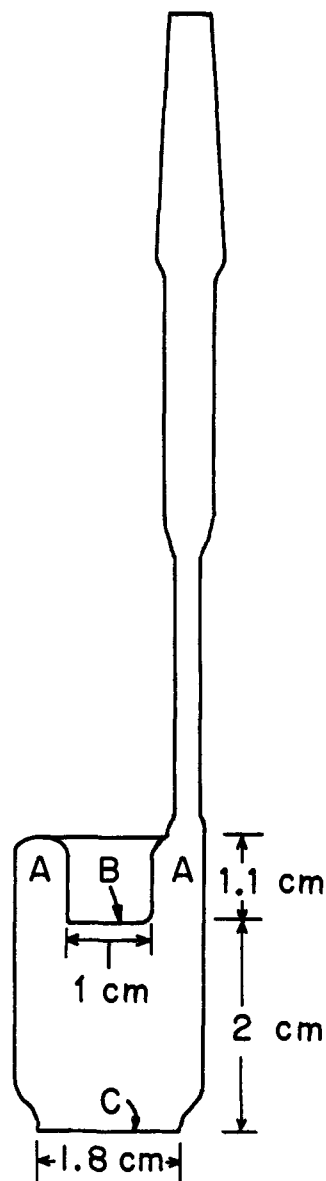


Figure 1. Cell for Bendix polarimeter: A, free volume; B, upper window; C, lower window.

more recrystallizations were carried out in a similar way. Each time the solid was dissolved in 500 ml of warm 95% ethanol under nitrogen and when the solution cooled to room temperature approximately 500 ml of ether was added slowly: yield after crystallizations, 141 g; mp 111–117°;  $[\alpha]_{D}^{26}$   $-217.7^\circ$  (*c* 0.150 g/10 ml of ethanol).

The tartrate salt (138.3 g) was dissolved in a minimum amount of water (510 ml) and 500 ml of ether was added. To the solution which was stirred vigorously and cooled by an ice bath, a solution of 36.8 g of sodium hydroxide in 150 ml of water was added dropwise. The rate of addition was such that the temperature remained below 20°. The ether layer was removed and the water layer extracted with three 250-ml portions of ether. The combined ether layers were washed with 300 ml of saturated aqueous sodium chloride. The remaining solution was filtered through anhydrous potassium carbonate above a filter and then dried overnight over anhydrous potassium carbonate. After evaporation of the solvent there remained 54 g of crude (–)-*N*-methyl-*N'*- $\alpha$ -phenylethylhydrazine. An nmr spectrum indicated that a substantial degree of oxidation to the corresponding azo compound had taken place so the crude hydrazine was dissolved in 400 ml of *n*-pentane and slowly treated with 108 g of yellow mercuric oxide while the solution was kept below 25°. After two hours the mixture was filtered and the solvent evaporated. (–)-Methylazo- $\alpha$ -phenylethane distilled at 24–25° (0.25 mm): yield 42 g;  $[\alpha]_{D}^{26}$   $-144.3^\circ$

(*c* 0.04141 g/5 ml of abs ethanol). The uv and nmr spectra are in accord with those previously published.<sup>2a</sup>

**Kinetics.** The rate of decomposition of the azo compound at  $161.90 \pm 0.08^\circ$  was followed in two ways: (a) measuring the rate of increase of gas pressure in an all-glass system described previously,<sup>2c</sup> and (b) measuring the rate of loss of optical activity in a Bendix Polarimeter, Model 143 A, with cells thermostated to  $161.90 \pm 0.15^\circ$ . Both thermostats were standardized to the same temperature by using the same thermocouple which in turn was calibrated with an NBS thermometer.

The polarimeter thermostat was fabricated from an aluminum block  $8.5 \times 3.2 \times 5.7$  cm. Two 1-cm diameter vertical holes were drilled about 4 cm apart. Concentric with these holes, two 2.5-cm diameter holes were drilled from the bottom and only 4 cm deep. Into these cylindrical channels were placed aluminum cylindrical cell holders which were held in place by set screws. Cartridge heaters, placed in precut channels, received power from a Cole-Parmer Versa-Therm proportional electronic temperature controller, Model 2156. A thermistor, embedded in the block, served as the input and sensing device of the controller. The block was separated from the polarimeter by a Teflon plate and the polarimeter was cooled by circulating tap water through a jacket. In trial runs the temperatures inside a polarimetric cell and of the block were monitored with thermocouples and the settings on the controller adjusted so that the temperature inside the cell was the same as in (a) (*vide supra*). During kinetic runs the temperature of the block was monitored with its thermocouple.

A typical quartz polarimeter cell is shown in Figure 1. The cell was generally filled to within a few millimeters of its upper window. At higher temperatures the liquid expanded and covered the bottom face of the top window but still left free space in the top portion of the cell (region A). In this way, the nitrogen evolved during the reaction did not accumulate at the top window but migrated to the top portion of the cell. In a typical run, 0.0203 g of optically azo compound was dissolved in 4 ml of hydrocarbon solvent. Then 3.4 ml of this solution was added to the cell. The cell was connected to a high vacuum line and the contents degassed by standard techniques. The cell was sealed with a torch at this point. All handling was carried out with the contents shielded from the light by a black cloth. Prior to the start of a run, the cell was placed in an oven, maintained, at about 100°, for about 0.5 hr and then immediately transferred to the thermostated block maintained at 162°. The block was then placed inside the polarimeter. The block also accommodated a standard cell at the same temperature. The cell containing the azo compound was allowed to remain in the path of the light beam during the run but the light was blocked by a Teflon sheet when readings were not taken. Readings in the standard cell were taken before and after the run to insure that the polarimeter maintained stability. The output of the polarimeter was connected to a variable 100 ohm resistor and the voltage across this resistor was monitored with an Orion digital voltmeter Model 801. Readings were taken by removing the Teflon strip for 0.8 min at which time the polarimetric reading stabilized. A similar run at room temperature was carried out.

Nonlinear least-squares solutions of the kinetic data from both types of runs were obtained as described previously.<sup>2b</sup>

**Viscosity** measurements were made in Ostwald viscosimeter in a thermostated oil bath. The viscosimeter was calibrated with methanol and benzene at 29° and that cell constant was used at 161.9° for the measurement of hexadecane–hexamethylbenzene and Nujol–hexadecane–hexamethylbenzene solvents. The densities of the latter two solvent mixtures were determined by using the viscosimeter as a pycnometer. The viscosities of the hexadecane–HMB (last entry of Table I) and Nujol–hexadecane–HMB (last entry of Table II) solvents at 161.9° are 0.420 and 1.08 cP, respectively.

## Results

*N*-Methyl-*N'*- $\alpha$ -phenylethylhydrazine was resolved by repeated recrystallization of the *d*-tartrate salt and the optically active azo compound ( $[\alpha]_{D}^{26}$   $-144.3^\circ$ ) was obtained through oxidation of the substituted hydrazine. Both the rate of loss of optical activity of the resolved azo compound and the rate of nitrogen production from the racemic compound were measured at 161.9° in the same solvents, hexadecane and Nujol. In addition, the rates were determined in solutions of

**Table I.** First-Order Rate Constants for Loss of Optical Activity and Appearance of Nitrogen during Thermal Decomposition of Methylazo- $\alpha$ -phenylethane in Hexadecane at 161.9°

Weight per cent		[HMB]/[I] <sup>a</sup>	10 <sup>4</sup> k <sub><math>\alpha</math></sub> , sec <sup>-1</sup>	10 <sup>4</sup> k <sub>N<sub>2</sub></sub> , sec <sup>-1</sup>	k <sub><math>\alpha</math></sub> /k <sub>N<sub>2</sub></sub>
[I]	[HMB]				
0.954	0	0	1.75 ± 0.03		
1.257	0	0	1.77 ± 0.03		
0.661	0	0	1.67 ± 0.02		
0.526	0	0		1.523 ± 0.02	
0.528	0	0		1.523 ± 0.02	
		0			1.13 <sub>6</sub>
0.933	10.79	10.6	1.34 ± 0.01		
0.930	17.69	17.4	1.26 ± 0.01		
0.659	6.52	9.04	1.34 ± 0.01		
0.656	6.51	9.07		1.248 ± 0.002	
		9.05			1.07
0.605	10.24	15.5	1.27 ± 0.01		
0.605	10.28	15.5		1.223 ± 0.002	
0.604	10.28	15.5		1.235 ± 0.002	
		15.5			1.03 <sub>3</sub>
0.577	12.36	19.6	1.24 ± 0.01		
0.577	12.36	19.6		1.219 ± 0.001	
		19.6			1.02 <sub>0</sub>
0.573	13.62	21.7	1.23 ± 0.01		
0.572	13.61	21.7		1.213 ± 0.002	
0.573	13.61	21.7		1.213 ± 0.001	
		21.7			1.01 <sub>4</sub>

<sup>a</sup> Molar ratio of hemethylbenzene to methylazo- $\alpha$ -phenylethane.

**Table II.** First-Order Rate Constants for Loss of Optical Activity and Appearance of Nitrogen during Thermal Decomposition of Methylazo- $\alpha$ -phenylethane in Nujol at 161.9° <sup>a</sup>

Weight per cent		[HMB]/[I] <sup>b</sup>	10 <sup>4</sup> k <sub><math>\alpha</math></sub> , sec <sup>-1</sup>	10 <sup>4</sup> k <sub>N<sub>2</sub></sub> , sec <sup>-1</sup>	k <sub><math>\alpha</math></sub> /k <sub>N<sub>2</sub></sub>
[I]	[HMB]				
0.519	10.21	17.9	1.23 ± 0.01		
0.519	10.21	17.9		1.181 ± 0.001	
		17.9			1.04
0.515	11.94	21.2	1.21 ± 0.01		
0.515	11.94	21.2		1.163 ± 0.001	
		21.2			1.04
0.496	13.30	24.5	1.20 ± 0.01		
0.496	13.30	24.5		1.164 ± 0.001	
0.496	13.3	24.5		1.165 ± 0.001	
		24.5			1.03

<sup>a</sup> Solvent: 90% Nujol, 10% hexadecane. <sup>b</sup> Molar ratio of hexamethylbenzene to methylazo- $\alpha$ -phenylethane.

varying concentrations of hexamethylbenzene. The raw kinetic data of about 80–90 points, taken over at least 90% reaction for each run, was fitted to a first-order rate law using a nonlinear least-squares program.<sup>2b</sup>

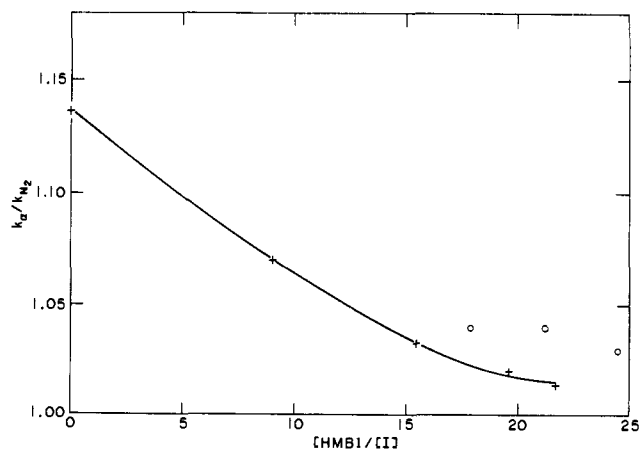


Figure 2. Thermal decomposition of methylazo- $\alpha$ -phenylethane. Ratio of polarimetric to nitrogen evolution rate constants as a function of the ratio of hexamethylbenzene to azo compound. Crosses refer to hexadecane and circles to Nujol.

The rate constants are shown in Tables I and II and in Figure 2. The standard deviations in individual rate constants are generally less than 1% for the loss of optical activity and 0.1% for nitrogen evolution.

Although the two methods required different thermostats, they were adjusted so that the two kinetic systems were at the same temperature to within 0.01°. The thermocouple, used to measure the temperature within the polarimetric cell, was also used to measure the temperature of the oil bath thermostat containing a stirred reaction flask as part of the system used to measure the rate of nitrogen evolution.

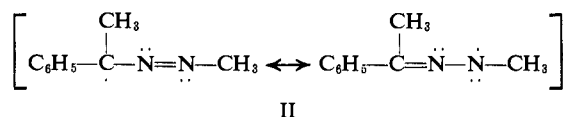
## Discussion

During the course of this work, the preparation of (–)-benzylazo- $\alpha$ -phenylethane from (–)-*N*-benzyl-*N'*- $\alpha$ -phenylethylhydrazine, resolved through its *d*-camphorate salt, was reported.<sup>5a</sup> To our knowledge this work and the present study are the only two cases where optically active azo compounds have been prepared through resolution of the precursor hydrazine. Previous examples have involved the coupling of optically active amines,<sup>5b,6ab</sup> the formation of monosubstituted

(6) (a) P. D. Bartlett and J. M. McBride, *Pure Appl. Chem.*, **15**, 89

hydrazines from resolved amines,<sup>5a</sup> or the addition of substituted hydrazines to optically active ketones.<sup>6c</sup> Although direct resolution of unsymmetrical hydrazines appears to be an attractive route to optically active unsymmetrical azo compounds it may be limited by the weakly basic nature of some of the more hindered substituted hydrazines.<sup>7</sup>

The rate of loss of optical activity has been compared with the rate of nitrogen appearance in two solvents of different viscosity. In the majority of kinetic runs the concentration of azo compound is approximately 0.6% or about 0.03 *M*. Judging from previous published experiments on hydrogen transfer from solvent to alkyl radical it might have been argued that this low concentration of azo compound might have been sufficient to ensure a unimolecular mechanism for loss of optical activity. The results with hexamethylbenzene (HMB),<sup>8</sup> a good hydrogen donor, suggest that in the absence of HMB, there appears to be a minor pathway for racemization even at 0.03 *M* methylazo- $\alpha$ -phenylethane. Methyl or hexadecyl radical might abstract benzylic hydrogen from (-)-I to give II which in turn might



abstract hydrogen from solvent and lead to nitrogen evolution *via* ( $\pm$ )-I.<sup>9</sup> HMB appears to intercept the radical that attacks I. As the ratio of HMB to I increases, both the rate of nitrogen evolution and loss of optical activity decreases. The viscosity of pure hexadecane at 161.9° is 0.48 cP.<sup>10</sup> The addition of HMB lowers the viscosity but only slightly. At the highest concentration used where HMB accounts for 14% by weight of the total solvent, the measured viscosity is 0.42 cP (see Experimental Section). The diminution of both the loss of optical activity and nitrogen evolution rates with increasing HMB in the solvent cannot reasonably be attributed to a solvent viscosity effect since only a modest change in the individual rates are observed when the reaction is carried out in Nujol-hexadecane-HMB where the viscosity is about twice as large as in the hexadecane-HMB solvent. It seems more reasonable, however, to suggest that the effect of HMB in these solvents is the result of a chemical interaction, such as a scavenger, rather than a physical one.

The possibility that HMB stabilizes azomethyl radicals and/or  $\alpha$ -phenylethyl radicals through solvation or  $\pi$  complexation<sup>11</sup> should be considered. Increased stability might result in a retardation of return and decomposition of the azomethyl radical. In a recent study of the thermal decomposition of azocumene, Nelsen and Bartlett<sup>12</sup> observed that the rate ratio of

(1967); (b) D. J. Severn and E. M. Kosower, *J. Amer. Chem. Soc.*, **91**, 1710 (1969); (c) J. R. Buckingham and R. D. Guthrie, *Chem. Commun.*, 1241 (1967).

(7) Joanna Fowler, unpublished observations, 1970.

(8) The high temperature of this study prevents the use of many of the more common scavengers because of their thermal instability. Quinones, while efficient at this temperature as methyl scavengers, render the solution rather opaque to the polarimeter.

(9) In previous experiments<sup>2d</sup> with I, the minimum amount of nitrogen gas recovered in a scavenging solvent is  $98.5 \pm 0.8$  mol %. The value originally given in reference 2d is in error.

(10) F. D. Rossini, Ed., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Materials," API Project 44, Carnegie Press, Pittsburgh, Pa., 1952, Table 20c.

(11) E. S. Huyser, *Advan. Free Radical Chem.*, **1**, 77 (1965).

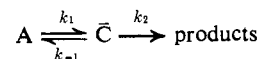
diffusion to the sum of coupling and disproportionation of caged cumyl radicals increases in the  $\pi$ -base solvents, toluene and benzene, but decreases in nitrobenzene and chlorobenzene. These effects, which are corrected for differences in viscosity, have been suggested to be the result of a solvent retardation of diffusion, strongest in nitrobenzene, or caged radical stabilization by solvation, most predominant in toluene. The assignment of the more dominant role of solvent has not been made.

It would appear that HMB acting in the present system by either solvation mechanism would lead to an *enhanced* rate of nitrogen evolution. If HMB were to affect the diffusion rate it would be expected that diffusion would be enhanced in the HMB-hexadecane solvent relative to pure hexadecane. Alternatively, if the addition of HMB were to stabilize caged radicals, both return ( $k_{-1}$ , eq 2) and decomposition within the cage ( $k_2$ ) would be retarded and also lead to a more rapid rate of nitrogen evolution. The possibility that HMB only impedes decomposition within the cage but does not retard return is denied by our observations (Figure 2). Our data, indicating a slower rate of nitrogen evolution in mixed HMB solvents, run opposite to the rate effects predicted above and appear to rule out specific solvation of diffusion or caged radicals. It is more likely that the rate retardation in the presence of HMB is due to scavenging of methyl radicals and the prevention of induced decomposition and/or results from solvent stabilization of the reactant azo compound.

The solvent effect is cancelled out when a ratio of the two rate constants is obtained as can be seen from the Tables and Figure 2. This ratio decreases and appears to level out at about 1.01 for hexadecane and 1.03–1.04 for Nujol.<sup>13</sup> The plateaus of the rate constant ratio *vs.* the [HMB]/[I] ratio are reached at rather high concentrations of hexamethylbenzene so the solvents are no longer pure hexadecane or Nujol but mixtures of these and the scavenger.

The kinetic scheme for loss of nitrogen can be written as

Scheme I



and by steady-state treatment yields

$$[A] = [A]_0 e^{-(k_1 k_2 / k_{-1} + k_2)t} \quad (3)$$

where  $t$  is the time and  $\bar{C}$  refers to caged  $\alpha$ -phenylethyl and azomethyl radicals.  $k_2$  represents all processes leading to products, *i.e.*, diffusion and decomposition within the cage. If the rate constant for nitrogen loss is defined as  $k_{N_2}$  then

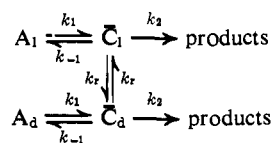
$$k_{N_2} = \frac{k_1 k_2}{k_{-1} + k_2} \quad (4)$$

A similar kinetic scheme with the same notation can be written for the decomposition and racemization of (-)-I (Scheme II). Here  $A_l$  and  $A_d$  refer to levo and dextro azo compound and  $\bar{C}_l$  and  $\bar{C}_d$  are enantiomeric

(12) S. F. Nelsen and P. D. Bartlett, *J. Amer. Chem. Soc.*, **88**, 143 (1966).

(13) After 50% decomposition in Nujol the remaining azo compound is less than 2.5% racemized and therefore the demonstration of return by the isolation of racemized azo compound from these dilute solutions would not appear to be as precise as the kinetic method used here.

## Scheme II



caged geminate radicals. Even though the  $\alpha$ -phenylethyl radical is probably planar, chirality can be maintained by the inability of the plane containing the central atoms of the  $\alpha$ -phenylethyl radical to flip with respect to the azomethyl radical. Inversion of the  $\alpha$ -phenylethyl radical can be achieved by interchanging  $\text{CH}_3$  and hydrogen groups through rotation about the benzylic-carbon-phenyl-carbon bond. In this way only a minimum amount of solvent molecules have to be reoriented.

Equation 5 can be derived from Scheme II if the

$$\frac{dx}{dt} = - \left[ k_1 - k_1 k_{-1} \frac{k_{-1} + k_2}{(k_{-1} + k_2 + k_r)^2 - k_r^2} \right] x \quad (5)$$

steady-state assumption is made for  $\bar{C}_1$  and  $\bar{C}_d$ . The equation describes a first-order rate process under all conditions where  $x = [A_1] - [A_d]$ . The observed rate constant,  $k_\alpha$ , for loss of optical activity is that shown in eq 6. Values of  $k_\alpha$  and  $k_{N_2}$  were determined under

$$k_\alpha = k_1 \left[ 1 - k_{-1} \frac{k_{-1} + k_2}{(k_{-1} + k_2 + k_r)^2 - k_r^2} \right] \quad (6)$$

identical conditions; it is instructive to compare the two. If  $k_\alpha$  is divided by  $k_{N_2}$ , eq 7 is obtained.  $k_\alpha$  will

$$\frac{k_\alpha}{k_{N_2}} = \frac{k_{-1} + k_2}{k_2} \left[ 1 - k_{-1} \frac{k_{-1} + k_2}{(k_{-1} + k_2 + k_r)^2 - k_r^2} \right] \quad (7)$$

always be greater than or equal to  $k_{N_2}$ . If the observed ratio ( $k_\alpha/k_{N_2}$ ) is expressed as  $1 + \Delta$  and the substitutions,  $r = k_r/k_{-1}$  and  $b = k_{-1}/k_2$ , are made, eq 7 can be simplified to yield

$$r = \frac{1}{2b} \left[ \frac{1 + 1/b}{1/\Delta - 1/b} \right] \quad (8)$$

It can be seen from eq 8 that the minimum branching ratio ( $b$ ) of return ( $k_{-1}$ ) to completion of reaction ( $k_2$ ) is equal to  $\Delta$ . This is so when  $r$  approaches infinity. If  $r$  is small, however, a larger value of  $b$  is required for the same observed  $\Delta$ . Return cannot be demonstrated if caged radicals do not racemize (*i.e.*, when  $r \rightarrow 0$ ).

Unfortunately, an independent solution for  $b$  cannot be obtained but requires a knowledge of  $r$  in addition to the experimentally determined  $\Delta$ . The dependence of  $b$  on different values of  $r$  is shown in Figure 3 for two values of  $\Delta$ . Some thoughts on the magnitude of  $r$  follow.

Starting with azobis- $\alpha$ -phenylethane, Greene and co-workers<sup>5b</sup> have been able to determine the ratio of rates of rotation to combination of caged  $\alpha$ -phenylethyl radicals. At  $105^\circ$  in benzene, the  $\alpha$ -phenylethyl radical rotates, with respect to its caged partner, about 14 times faster than it combines with another of its kind in

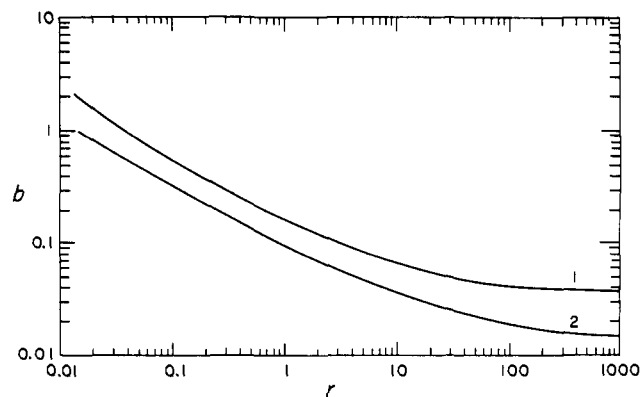


Figure 3. The dependence of  $b$  on  $r$  (eq 8): curve 1,  $\Delta = 0.037$ ; curve 2,  $\Delta = 0.015$ .

the cage. Kopecky and his coworkers<sup>5a</sup> have carried out a parallel study with benzylazo- $\alpha$ -phenylethane and found that rotation is about 11 to 16 times faster than cage combination in a variety of solvents at a similar temperature. In both of these cases, admittedly, a nitrogen molecule is interposed between caged radicals retarding rapid combination. But even when there is no insulating molecule between radicals rotation may be rapid compared with combination. The intermediate diradical from the  $2 + 2$  addition of 1,1-dichloro-2,2-difluoroethylene to different isomers of 2,4-hexadiene rotates about ten times faster than it cyclizes.<sup>14</sup> Although radical centers are in close proximity, cyclization may be somewhat slower than combination of caged radicals because of the repulsions developed in the cyclobutyl transition state. Since radical-radical combination is expected to have a near zero activation energy, higher temperatures will favor an increase of rotation relative to combination of radicals. This appears to be borne out by the isomer distribution from the  $2 + 2$  reaction at  $80$  and  $100^\circ$ .<sup>14</sup> Therefore, at  $161^\circ$  we might expect the  $\alpha$ -phenylethyl radical to undergo considerable rotation in our system before cage combination with the azomethyl radical occurs and we might expect  $r$  to have a value of about 10 to 16.

During thermal decomposition the optical activity of  $(-)$ -I as a function of time assumes a good first-order decay curve (see Results) with rate constants shown in Tables I and II. In these Tables are also first-order rate constants for the decomposition of I obtained by following the appearance of nitrogen. From the  $k_\alpha/k_{N_2}$  ratio, assuming a value of  $r$  between 10 and 16 and independent of viscosity, we obtain  $b$  equal to 0.032 to 0.036 in hexadecane and 0.058 to 0.066 in Nujol. The results suggest that about one out of 30 caged radicals return in hexadecane while in Nujol return is twice as probable as in hexadecane.<sup>15</sup>

(14) L. K. Montgomery, K. Schueller, and P. D. Bartlett, *J. Amer. Chem. Soc.*, **86**, 622 (1964).

(15) Quantitative correlation of rates with viscosity data could, in theory, allow the dissection of  $k_2$  into its component parts. Since Nujol is an "atypical" paraffin<sup>33</sup> this correlation will not be attempted here.