

Cage Effects and the Viscosity Dependence of the Photolysis of Dibenzylamine and Tribenzylamine

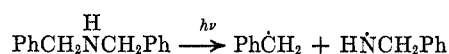
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The fates of the radical pairs formed in the photolytic decomposition of *N,N*-dibenzylamine and *N,N,N*-tribenzylamine in solution are examined. Viscosity of the medium is used to probe a model for the "cage effect," in which radicals suffer competition among recombination, diffusion, and reaction with the solvent or amine.

The photolytic decomposition of amines serves as a model for the reaction of alkylamino radicals in solution. The product study of the photolysis of *N,N*-dibenzylamine presented in the foregoing paper¹ is accommodated by an initial homolysis of the benzyl-nitrogen bond. The benzylamino and dibenzylamino



radicals are involved in subsequent dark reactions following the photodissociation of *N,N*-dibenzylamine. In this study we examine the viscosity dependence of the quantum yield for reaction, in an attempt to obtain a more quantitative understanding of the initial reactions. The results are compared with the photolysis of *N,N,N*-tribenzylamine and interpreted in terms of a model for the "cage effect," in which the fate of the radical pair depends on the competition among recombination, diffusion, and scavenging.²⁻¹⁹ Although the photochemistry of this system is also of interest, we are concerned here primarily with the thermal reactions subsequent to homolysis.

Results and Discussion

The quantum yields were determined for reactions allowed to reach no more than 0.1% completion (see Experimental Section). In two cases, 0.1 and 1.0 *M* dibenzylamine in cyclohexane, the value was taken from the slope of a line obtained by plotting the yield of benzylamine as a function of time. Problems associated with filtering due to the formation of imine were avoided by this method. The quantum yields obtained in this manner are listed in Table I and plotted as a function of dibenzylamine concentration in Figure 1. All quantum yields were obtained at one lamp

TABLE I

QUANTUM YIELD FOR BENZYLAMINE FORMATION AT 253 nm (PhCH ₂) ₂ NH ^a concn	Φ(PhCH ₂ NH ₂)
0.02	0.025 ± 0.002
0.05	0.036 ± 0.002
0.10	0.061 ± 0.004
0.30	0.093 ± 0.002
0.50	0.112 ± 0.009
0.70	0.123 ± 0.003
0.90	0.129 ± 0.001
1.00	0.137 ± 0.011
1.50	0.141 ± 0.001
2.00	0.141 ± 0.003
2.50	0.139 ± 0.006
3.00	0.140 ± 0.001

^a Molar concentration in cyclohexane. ^b Error limits are average deviations based on from four to eight separate determinations.

intensity. The possible dependence of the quantum yield on the intensity of irradiation was not investigated.

The C-N bond strength in dibenzylamine is approximately 55 kcal mol⁻¹ based on the trend observed with other amines²⁰ and the value of 59.8 kcal mol⁻¹ for benzylamine.²¹ During photolysis at 254 nm, the energy in excess of that required to break the bond (~60 kcal mol⁻¹) is partly partitioned as translational energy to separate the two fragments.²²⁻²⁴ If the particles recombine before they have diffused more than one molecular diameter from each other, the process becomes kinetically equivalent to thermal deactivation of an excited state.²⁵ This result has been termed "primary recombination."¹⁸ Prior to recombination, there may or may not be a residual interaction between the radical fragments, *i.e.*, the motion of one may influence the motion of the other. If, however, the fragments escape the primary recombination, they can diffuse independently of one another and at distances from one to two molecular diameters apart.¹⁸ If recombination then occurs between these original partners the process is known as "secondary recombination,"¹⁸ which may be more generally expressed to include all recombinations of original (geminate) partners which have not had time to reach a statistical distribution in solution as a result of random diffusion. If, at the same time, a scavenger(s) is present which is capable of reacting with one of the radicals formed in the

- (1) M. A. Ratcliff, Jr., and J. K. Kochi, *J. Org. Chem.*, **37**, 3268 (1972).
- (2) J. Franck and E. Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934).
- (3) S. Kodama, *Bull. Chem. Soc. Jap.*, **35**, 652, 658, 824, 827 (1962).
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- (5) K. Chakravorty, J. M. Pearson, and M. Szwarc, *ibid.*, **90**, 283 (1968).
- (6) M. Feld and M. Szwarc, *ibid.*, **83**, 2998 (1961).
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- (8) P. D. Bartlett and S. F. Nelson, *ibid.*, **88**, 139 (1966).
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- (10) T. Koenig and M. Deinzer, *ibid.*, **90**, 7014 (1968).
- (11) T. Koenig, J. Huntington, and R. Cruthoff, *ibid.*, **92**, 5409 (1970).
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- (16) J. R. Nash, R. R. Williams, Jr., and W. H. Hamill, *ibid.*, **82**, 5974 (1960).
- (17) H. A. Gillis, R. R. Williams, Jr., and W. H. Hamill, *ibid.*, **83**, 17 (1961).
- (18) (a) R. M. Noyes, *ibid.*, **77**, 2042 (1955). (b) For a recent discussion see also D. L. Bunker and B. S. Jacobson, *ibid.*, **94**, 1843 (1972).
- (19) O. Dobis, J. M. Pearson, and M. Szwarc, *ibid.*, **90**, 278 (1968).

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- (21) M. Szwarc, *Proc. Roy. Soc., Ser. A*, **198**, 285 (1949).
- (22) R. M. Noyes, *Z. Elektrochem.*, **64**, 153 (1960).
- (23) D. Booth and R. M. Noyes, *J. Amer. Chem. Soc.*, **82**, 1868 (1960).
- (24) J. Franck and E. Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934).
- (25) J. Jortner, M. Ottolenghi, and G. Stein, *J. Phys. Chem.*, **66**, 2029 (1962).

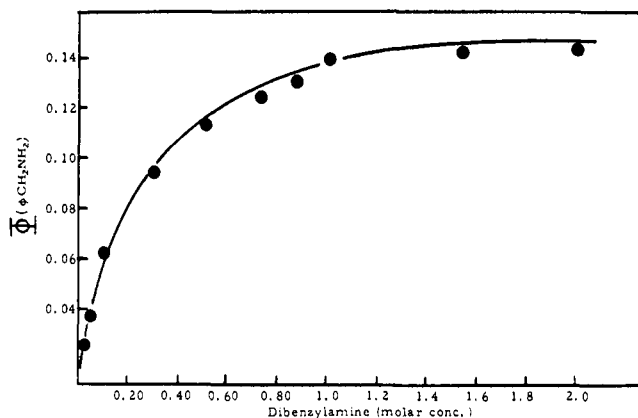


Figure 1.—Quantum yield of benzylamine formation vs. the concentration of dibenzylamine.

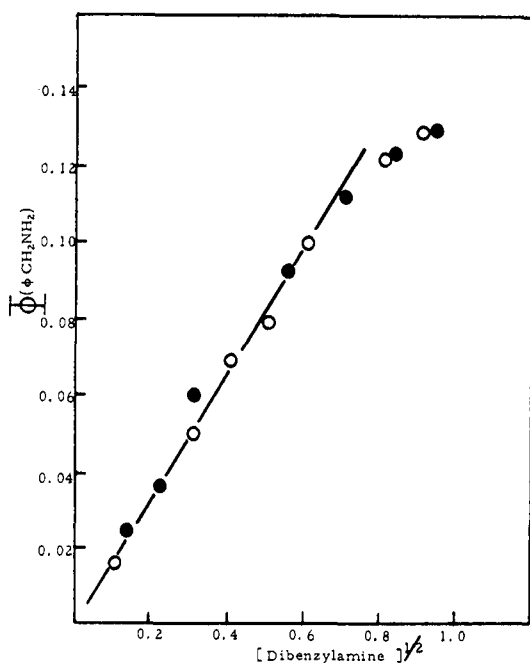
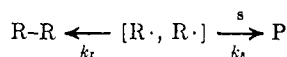


Figure 2.—Quantum yield of benzylamine formation vs. the square root of the concentration of dibenzylamine: (●) experimental; (○) taken from curve in Figure 1.

dissociation, it may compete with the secondary recombination step. Such a competition can be seen as a partitioning between two processes represented by k_r ,



the rate constant for secondary recombination, and k_s , the rate constant for scavenging of the geminate radical pair.

Noyes has treated the kinetics of this scavenging process in a series of papers.^{18,26} The lifetime of the cage reaction (secondary recombination) is best viewed as the time interval during which there is a finite probability for the pair to recombine.²⁷ At times greater than this, the probability for the reencounter of original partners becomes negligible. Noyes obtained an ex-

(26) (a) R. M. Noyes, *J. Amer. Chem. Soc.*, **78**, 5486 (1956); (b) H. Rosman and R. M. Noyes, *ibid.*, **80**, 2410 (1958); (c) R. M. Noyes, *Z. Elektrochem.*, **64**, 153 (1960); (d) R. M. Noyes, *J. Phys. Chem.*, **65**, 763 (1961).
(27) W. Braun, L. Rajenbach, and F. R. Eirich, *J. Phys. Chem.*, **66**, 1591 (1962).

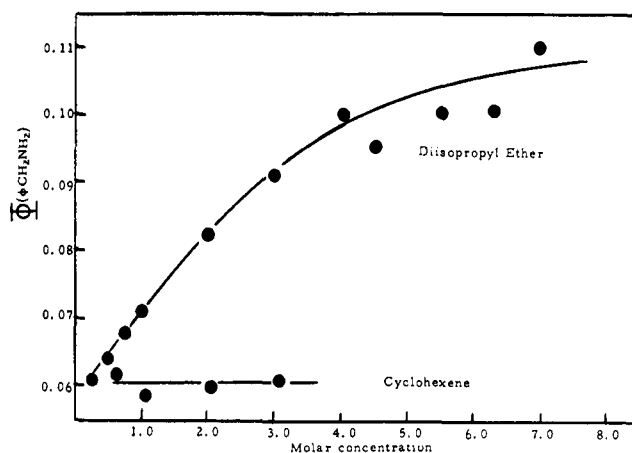


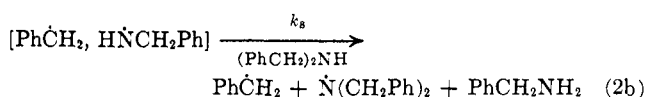
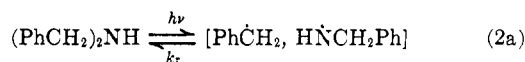
Figure 3.—Quantum yield of benzylamine formation vs. the concentration of potential scavengers.

pression (eq 1) relating the quantum yield to the square root of scavenger concentration,²⁸ where Φ is the ob-

$$\Phi = \Phi_r + C(S)^{1/2} \quad (1)$$

served quantum yield, S is the scavenger concentration, and C is a term containing molecular parameters to be discussed later. The term Φ_r was described by Jortner²⁵ as the "residual yield," and defined as the quantum yield in the presence of scavenger at concentrations sufficient to prevent recombination from bulk solution, but too low to compete with secondary recombination.

For the photolysis of dibenzylamine this effect can be described as a competition between k_r and k_s (eq 2),



in which k_r represents return to starting material and k_s that leading to products. A plot of $\Phi(\text{PhCH}_2\text{NH}_2)$ vs. $[(\text{PhCH}_2)_2\text{NH}]^{1/2}$ is shown in Figure 2. Above concentrations of approximately 0.5 M in amine, however, the plot deviates greatly from linearity. At the higher concentrations, dibenzylamine may exist as hydrogen-bonded aggregates which could affect the measured quantum yields (*vide infra*).²⁹ The results are further complicated by the fact that the scavenger is also the photoreactive species.

Both cyclohexene and diisopropyl ether were examined as possible hydrogen donors, and each was expected to compete effectively with the dibenzylamine for the amino radicals. For two potential scavengers, eq 1 can be expanded to eq 3, where S' refers to either cyclohexene or diisopropyl ether. The results (Table II) for both cases are shown in Figure 3.

$$\Phi = \Phi_r + C(S)^{1/2} + C'(S')^{1/2} \quad (3)$$

That no effect was observed with cyclohexene was unexpected, but the dependence on diisopropyl ether concentration agrees with the relative reactivities of

(28) For a review see R. M. Noyes, *Progr. React. Kinet.*, **1**, 129 (1961).

(29) (a) Furthermore, approximations made during the derivation (*i.e.*, approximating an integral by a series expansion with the subsequent deletion of all but the first term) could cause deviations at higher scavenger concentrations.²⁸ (b) We wish to thank the referee for this suggestion.

TABLE II
THE EFFECT OF THE ADDITION OF CYCLOHEXENE AND
DIISOPROPYL ETHER ON $\Phi(\text{PhCH}_2\text{NH}_2)^a$

Cyclohexene			Diisopropyl Ether		
Concn ^b	$S^{1/2}$	$\Phi(\text{PhCH}_2\text{NH}_2)$	Concn ^b	$S^{1/2}$	$\Phi(\text{PhCH}_2\text{NH}_2)$
0.51	0.71	0.062	0.25	0.50	0.061
1.02	1.00	0.059	0.50	0.71	0.064
2.04	1.43	0.060	0.75	0.86	0.068
3.06	1.75	0.061	1.0	1.0	0.071
4.08	2.02	0.072	2.0	1.41	0.082
			3.0	1.73	0.091
			4.0	2.0	0.100
			4.5	2.12	0.095
			5.5	2.34	0.102
			6.26	2.50	0.104
			6.97	2.64	0.110

^a Solutions of 0.1 M in $(\text{PhCH}_2)_2\text{NH}$ irradiated at 25° with 253-nm radiation. ^b Molar concentration in cyclohexane.

the two reagents. For example, diisopropyl ether has been found to be approximately ten times as reactive as cyclohexene toward *n*-hexyl radicals,³⁰ but the relative reactivities toward benzylamino radical are unknown. A plot of the data according to eq 3 is shown in Figure 4.

In the derivation of eq 1, the constant, C , is given by $C = 2a\varphi\sqrt{\pi k_s}$, where a is a constant, k_s is the rate constant for scavenging, and φ is a term defined to be "the quantum yield of radical pairs escaping primary recombination."²⁹ From Fick's law, one can obtain an expression for the rate constant, k_s , applicable to steady-state diffusion (eq 4). This expression was suggested

$$k_s = 4\pi r_{AB} D_{AB} \quad (4)$$

by Noyes^{26a} and is similar to that obtained by Smoluchowski³¹ in his early treatments of diffusion-controlled reactions. In this expression, r_{AB} is the encounter distance between the potentially reacting species, and D_{AB} is the diffusion coefficient for their relative motion. In order for eq 4 to be strictly valid, however, the diffusion process must be the rate-limiting step.³² That the reaction under consideration meets these requirements is not obvious, although the reaction of the benzylamino radical with dibenzylamine should be exothermic. Furthermore, the photolysis yielded no material resulting from the dimerization of the benzylamino radical under conditions in which bibenzyl was readily detected.¹

The expression for k_s is introduced into eq 1 for purposes of testing the effect of viscosity changes on the quantum yield, by substituting the right-hand side of eq 4 and using a Stokes-Einstein relationship (eq 6),

$$\Phi = \Phi_r + 4\pi a\varphi\sqrt{[S]r_{AB}D_{AB}} \quad (5)$$

where k is Boltzman's constant and T the absolute temperature.³² If all terms but the viscosity and the

$$D_{AB} = \frac{2kT}{3\pi\eta r_{AB}} \quad (6)$$

scavenger concentration are constant, eq 7 predicts that the quantum yield will vary inversely with the square root of fluidity ($1/\eta$) at constant scavenger (*i.e.*, dibenzylamine) concentration.

$$\Phi = \Phi_r + C\sqrt{[S]/\eta} \quad (7)$$

(30) D. R. DeTar and D. V. Wells, *J. Amer. Chem. Soc.*, **82**, 5839 (1960).

(31) M. V. Smoluchowski, *Z. Phys. Chem.*, **92**, 129 (1917).

(32) A. M. North, *Quart. Rev., Chem. Soc.*, **20**, 421 (1966).

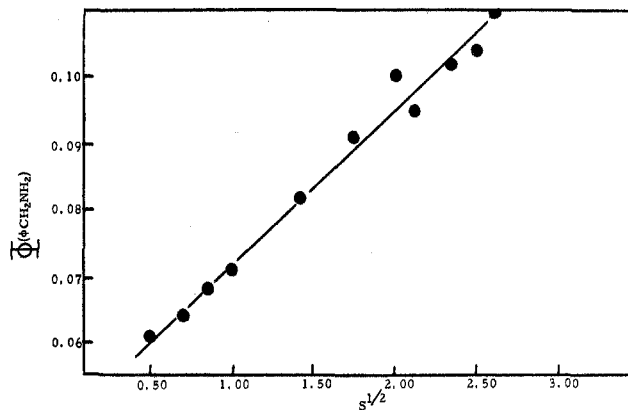


Figure 4.—Quantum yield of benzylamine formation vs. the square root of isopropyl ether concentration(s).

The quantum yield for the formation of benzylamine was measured in a series of hydrocarbon solvents of varying viscosity. The results (Table III) when

TABLE III
EFFECT OF VISCOSITY ON THE QUANTUM YIELDS OF
DIBENZYLAMINE PHOTOLYSIS

Solvent	D , g/ml	ν , cSt	η , cP	$\Phi(\text{PhCH}_2\text{NH}_2)$
Pentane	0.614	0.340	0.208	0.130
Hexane	0.648	0.441	0.285	0.111
Heptane	0.673	0.537	0.362	0.103
Isooctane	0.682	0.644	0.439	0.092
Nonane	0.708	0.856	0.606	0.078
Cyclohexane	0.767	1.028	0.788	0.061
Nujol (40%) ^a	0.757	2.214	1.676	0.044
Nujol (60%) ^a	0.793	5.164	4.095	0.027
Nujol (80%) ^a	0.828	15.84	13.11	0.018
Nujol (90%) ^a	0.852	32.27	27.49	0.006
DIPE (1.0) ^b	0.760	0.850	0.646	0.071
DIPE (2.0) ^b	0.757	0.730	0.553	0.082
DIPE (3.0) ^b	0.745	0.631	0.471	0.091
DIPE (5.0) ^b	0.731	0.501	0.367	0.103
DIPE (6.0) ^b	0.726	0.457	0.332	0.106

^a By volume, remainder is isooctane. ^b Concentration (M) of diisopropyl ether in cyclohexane.

plotted according to eq 7 give the predicted relationship (Figure 5). It can be seen that the quantum yield does approach zero as the viscosity increases.

The effect of diisopropyl ether was reinvestigated in light of this result, and the results are listed in Table III. The relationship between the quantum yield and the concentration of ether (Figures 3, 4) indeed appears to have been fortuitous, and the correlation is more adequately explained as a viscosity effect. The latter implies that neither cyclohexene nor diisopropyl ether reacted with the benzylamino radical as previously suggested. This conclusion may not be unwarranted due to the generally unreactive nature of alkylamino radicals³³⁻³⁵ and their apparent highly polar character.³⁶⁻³⁸

The product distribution for the photolysis of dibenzylamine was determined in several of the solvents

(33) B. R. Cowley and W. A. Waters, *J. Chem. Soc.*, 1228 (1961).

(34) D. Mackay and W. A. Waters, *J. Chem. Soc. C*, 813 (1966).

(35) K. M. Johnston, G. H. Williams, and H. J. Williams, *J. Chem. Soc. B*, 1114 (1966).

(36) E. L. O'Brien, F. M. Beringer, and R. B. Mesrobian, *J. Amer. Chem. Soc.*, **81**, 1506 (1959).

(37) R. S. Neale and E. Gross, *ibid.*, **89**, 6579 (1967).

(38) S. F. Nelson and D. H. Heath, *ibid.*, **91**, 6452 (1969).

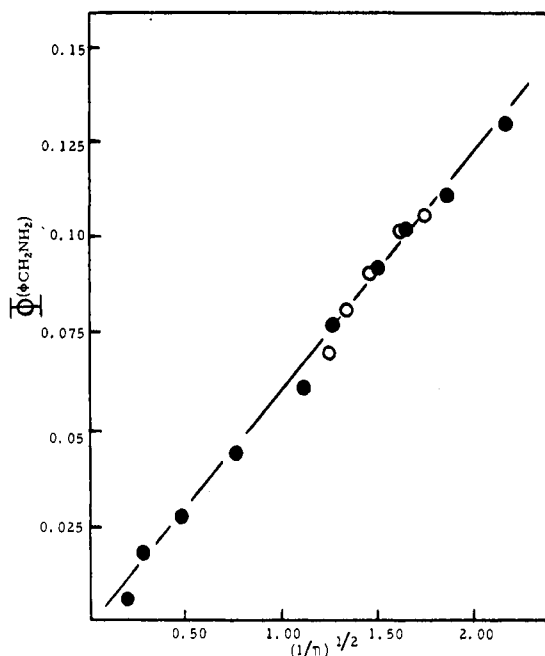


Figure 5.—Quantum yield of benzylamine formation vs. viscosity function: (●) hydrocarbon solvents; (○) isopropyl ether.

used for quantum yield studies in order to assure that the formation of benzylamine was not abnormally depressed relative to the other products by the nature of the solvent. As Table IV shows, the distribution

TABLE IV
PRODUCT DISTRIBUTION AS A FUNCTION OF
VISCOSITY AT 253 nm

Solvent	η , cP	Product, mmol				
		PhCH ₂ -NH ₂	PhCH=CH ₂	(Ph-CH ₂) ₂ NH	(Ph-CH ₂) ₂ N	(Ph-CH ₂) ₂
Pentane ^a	0.208	0.15	0.21	0.16	0.072	0.04
Hexane ^a	0.285	0.13	0.19	0.16	0.070	0.03
Heptane ^a	0.362	0.133	0.18	0.14	0.063	0.027
Isooctane ^a	0.439	0.138	0.17	0.14	0.060	0.024
Nonane ^a	0.606	0.13	0.14	0.12	0.050	0.02
Methanol ^a	0.498	0.06	0.04	0.07	0.02	0.01
Cyclohexene ^b	0.167	0.39	0.45	0.11		
Cyclohexane ^b	0.778	0.182	0.36	0.45	0.13	

^a Photolysis time, 60 min; (PhCH₂)₂NH 0.5 M. ^b Photolysis time, 300 min; (PhCH₂)₂NH 0.7 M.

of products remains more or less constant, the principal variation being in the absolute amounts produced. With the effect of viscosity clarified, the results obtained from varying the concentration of dibenzylamine in cyclohexane were investigated. Equation 7 can be rewritten as eq 8, and the quantum yield data

$$\Phi\eta^{1/2} = \Phi_r\eta^{1/2} + C(S)^{1/2} \quad (8)$$

(including the viscosities of the solutions of dibenzylamine in cyclohexane) are listed in Table V. A plot of the left-hand portion of eq 8 against the square root of the dibenzylamine concentration is shown in Figure 6. The term $\Phi_r\eta^{1/2}$ is zero by extrapolation of the amine concentration in Figure 2. The inability of eq 8 to predict the results may not be surprising considering the assumptions made. Nevertheless, some interesting observations can be made regarding the two apparently linear portions of the curve in Figure 6. Increasing the concentration of the amine has the effect of enhancing the quantum yield, whereas the accom-

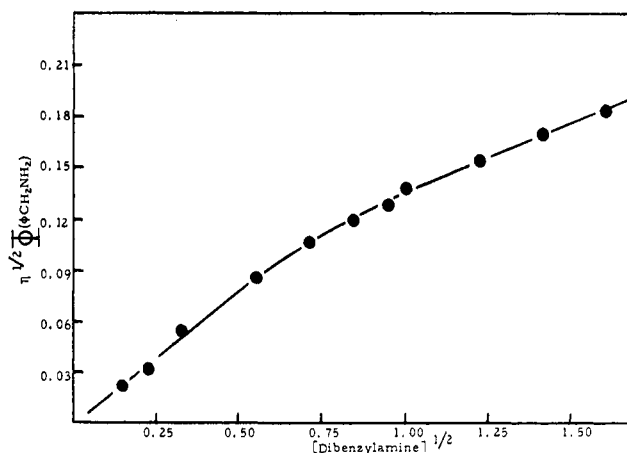


Figure 6.—Quantum yield dependence on both viscosity and molar concentration of dibenzylamine.

TABLE V
EFFECT ON QUANTUM YIELDS DUE TO VISCOSITY CHANGES
IN SOLUTIONS OF DIBENZYLAMINE IN CYCLOHEXANE

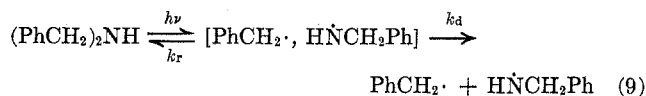
(PhCH ₂) ₂ NH, M	(S) ^{1/2}	η	$\Phi(\text{PhCH}_2\text{NH}_2)$	$\Phi\eta^{1/2}$
0.02	0.14	0.790	0.025	0.022
0.05	0.22	0.795	0.036	0.032
0.10	0.32	0.803	0.061	0.055
0.30	0.55	0.837	0.093	0.085
0.50	0.71	0.882	0.112	0.105
0.70	0.84	0.926	0.123	0.118
0.90	0.95	0.980	0.129	0.128
1.00	1.00	1.019	0.137	0.138
1.50	1.22	1.169	0.141	0.152
2.00	1.41	1.416	0.141	0.168
2.50	1.60	1.657	0.139	0.181
3.00	1.73	2.015	0.140	0.199

panying increase in the viscosity with concentration tends to reduce it. The lower part of the curve, between 0.02 and 0.7 M, is influenced largely by changes in the concentration. In this region the concentration changes by a factor of 35 while the viscosity increases by only 12%. Above approximately 0.9 M, the influence due to the viscosity change becomes important. Thus, from 1.0 to 3.0 M, the concentration of the amine changes by only a factor of 3 while the viscosity increases by over 100%. It is also important to recognize that, at the higher concentrations, the solvent cage surrounding the radical pair probably contains substrate molecules, especially if dibenzylamine is aggregated as hydrogen-bonded species. When the solvent cage has a high probability of containing one scavenger molecule, further increases in scavenger concentration should have little significance in terms of the foregoing expressions. Furthermore, the quantum yield should not show the same concentration dependence.³⁹

The effect due to viscosity, when considering the dual effect exerted on the quantum yield by increases in the concentration of dibenzylamine, can be discussed from an alternative point of view. Koenig has derived an equation which relates the rate constant for diffusive separation of a radical pair to the square root of fluidity.⁴⁰ This would correspond to k_d (eq 9) under

(39) A further test for eq 8 should involve studying the effect of changes in concentration at constant viscosity. This would eliminate problems associated with the probable viscosity dependence of the term C in eq 8.

(40) T. Koenig, *J. Amer. Chem. Soc.*, **91**, 2558 (1969).

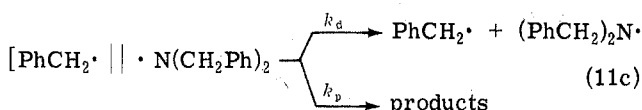
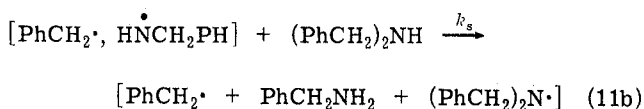
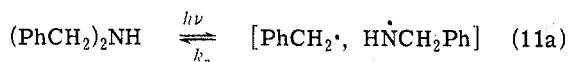


conditions in which a scavenger is not present. The radicals resulting from this diffusion process would have reached the point mentioned above in which the probability of geminate recombination has become negligible. A semiquantitative justification for the square root dependence was developed by Koenig,¹⁰ based upon the time dependence of k_d , which must compete with the return process k_r . He obtained the expression $k_d = r/(\rho - R_0)t$, where r is the root mean square displacement distance for a particle in a time t , ρ is an effective collision diameter, and R_0 is the initial distance of separation. Using the relationship $r = (2Dt)^{1/2}$, obtained from theories of Brownian motion, where D is the relative diffusion coefficient for the pair, he obtained the expression in eq 10 for k_d in units of sec^{-1} .

$$k_d = \left(\frac{2D}{t}\right)^{1/2} \frac{1}{\rho - R_0} \quad (10)$$

This expression predicts that k_d becomes smaller as the viscosity of the solution is increased. The effect due to the viscosity of dibenzylamine can be considered in this light. The radicals formed in the dissociative process can undergo many collisions with surrounding molecules before either diffusion or reaction has occurred.^{1, 18b, 41} If many collisions between the benzylamino radical and dibenzylamine occur for each reaction encounter, then for the nonreactive encounters the dibenzylamine has the same effect as any solvent, *i.e.*, to prevent the radical from escaping the "cage." An increase in the dibenzylamine concentration under these conditions increases the return process, k_r , by inhibiting the diffusion process, k_d .

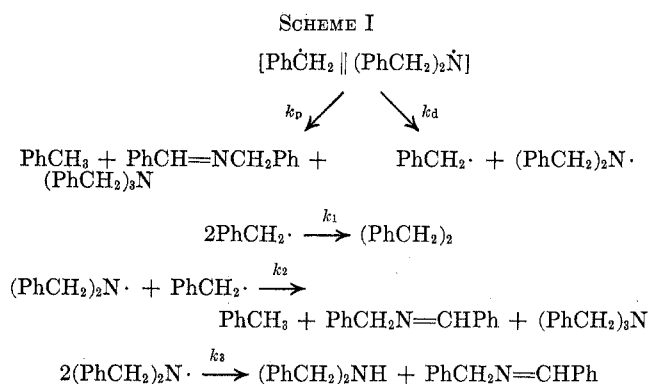
Following the initial dark reaction (*i.e.*, the abstraction of a hydrogen atom by the benzylamino radical), a pair of radicals remains which are also subject to reaction under "cage" conditions (eq 11). The effect



of reaction 11b is to produce a benzyl radical and a dibenzylamino radical under conditions where they are not statistically distributed throughout the solution.⁴² Therefore, the probability that these radicals will react with each other is greater than the probability that they will react with radicals of their own type. Once, however, diffusion has occurred, there is a statistical chance of encounter with either type of radical. Con-

sequently, for reaction 11c a distinction can be made between the process involving the benzyl radical and the dibenzylamino radical, which leads directly to products, and the diffusion process, which leads to the radicals being distributed evenly throughout the solution. Both events ultimately lead to the formation of toluene, tribenzylamine, and the imine, but bibenzyl can only be formed after the second event, *viz.*, diffusion.

If the formation of toluene occurs largely *via* this "quasi-cage" type of mechanism, the ratio of toluene ("cage" product) to bibenzyl ("noncage" product) should reflect k_d and should be affected by viscosity. The formation of products from the radical pair discussed in the model above is given in Scheme I. If



we assume that $k_1 = k_2/2 = k_3$ ⁴³ and the concentrations of benzyl and dibenzylamino radicals are the same, then a straightforward steady-state treatment gives the rates of formation of toluene and bibenzyl as $r[\text{PhCH}_3] = (3k_pA + 2k_dA)/3$ and $r[(\text{PhCH}_2)_2] = k_dA/3$, where $A = [\text{Ph}\dot{\text{C}}\text{H}_2 \parallel (\text{PhCH}_2)_2\dot{\text{N}}]$. Equation 12 results if the relative amounts of products are taken

$$\frac{\text{PhCH}_3}{(\text{PhCH}_2)_2} = \frac{3k_p}{k_d} + 2 \quad (12)$$

to represent the rate ratios. The rate constant k_d is assumed to be the only viscosity-dependent term,¹⁰ since k_p is the rate constant for reaction of the two species produced in the absence of bulk solvent effects. From eq 10 it follows that $\text{PhCH}_3/(\text{PhCH}_2)_2$ is proportional to $(1/D)^{1/2}$ or the square root of viscosity.

The data for this relationship are listed in Table VI.

TABLE VI
EFFECT OF VISCOSITY ON THE RATIO OF
TOLUENE TO BIBENZYL^a

$(\text{PhCH}_2)_2\text{-NH}^b$	$\frac{\text{PhCH}_3}{(\text{PhCH}_2)_2}$	$\eta^{1/2}$	Solvent ^c	$\frac{\text{PhCH}_3}{(\text{PhCH}_2)_2}$	$\eta^{1/2}$
0.20	5.0	0.86	Pentane	3.75	0.46
0.25	5.5	0.89	Hexane	4.3	0.54
0.50	7.0	0.94	Heptane	4.9	0.60
0.75	8.0	0.97	Isooctane	5.8	0.66
1.00	8.25	1.01	Nonane	6.3	0.78
1.50	9.5	1.08	Cyclohexane	7.0	0.88

^a Photolysis time, 60 min; 253 nm. ^b Molar concentration in cyclohexane. ^c 0.5 M $(\text{PhCH}_2)_2\text{NH}$.

(43) This may not be a valid assumption, however, since the self-reaction of amino radicals shows rather large steric effects. For example, the rate constant for diethylamino radicals is $7 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ at -90° , but for the isopropyl analog it is $5 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$ at -10° [J. R. Roberts and K. U. Ingold, *J. Amer. Chem. Soc.*, **93**, 6686 (1971)]. The rate of the cross-association of benzyl and dialkylamino would, however, be more similar to the dimerization of benzyl radicals.

(41) E. Rabinowitch and W. Wood, *Trans. Faraday Soc.*, **32**, 1381 (1936).

(42) The representation of the benzyl and dibenzylamino radical pair by the slash marks in eq 11c is to distinguish it from the initial pair in 11a. In a strict sense, the benzyl radical and dibenzylamino radical probably do not represent a "caged" pair; however, in our operational definition a "cage" is construed as a radical pair in a measurably nonstatistical distribution. Hydrogen bond aggregates should also be included in this context.

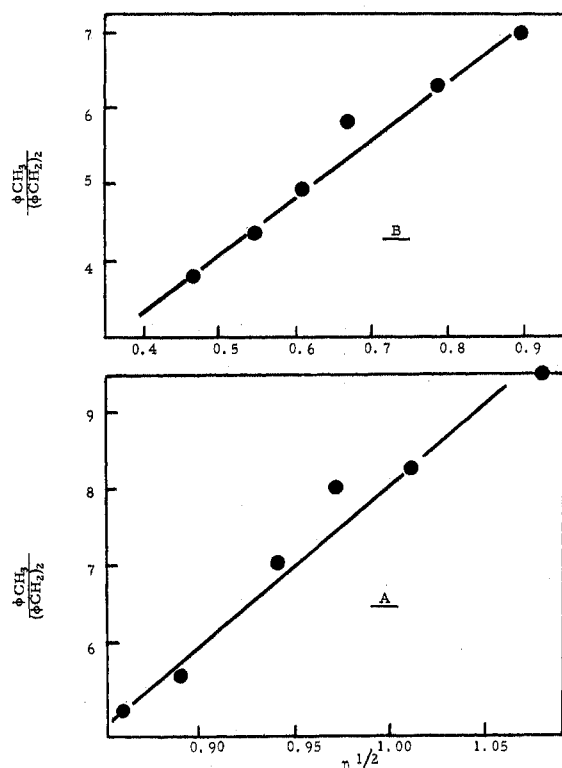


Figure 7.—Ratio of cage to noncage products vs. the viscosity: (A) dibenzylamine in cyclohexane; (B) hydrocarbon solvents.

As shown in Figure 7A for various concentrations of dibenzylamine in cyclohexane, the ratio of the two products does vary as predicted for the model being considered. Unlike the initial step in the reaction 11b where both viscosity and concentration were concerned, step 11c should show a linear relationship with the viscosity function alone. This linearity was found to hold, and in Figure 7B the same quantities are plotted for the data obtained in the series of hydrocarbon solvents. The slopes for the two plots are 8.3 and 21.6 for the hydrocarbon solvents and dibenzylamine, respectively. The higher value for the dibenzylamine is predictable, even though the viscosity effects of the two solutions may be similar. Thus, when dibenzylamine is the solvent, the reaction of the benzylamino radical with dibenzylamine (eq 11) (which is less available in the hydrocarbon solvent) results in the formation of the radical pair that is in closer proximity than that predicted by viscosity effects alone. Under these circumstances, there is a greater probability for encounter of the radical pair, and it is reflected in a higher ratio of "cage" to "noncage" products. The ratio of toluene to bibenzyl is only a crude measure of the cage effects, and additional studies of "cage" and "noncage" recombinations using stereochemical probes and chemically induced dynamic polarization would be desirable.

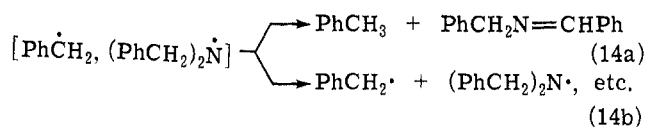
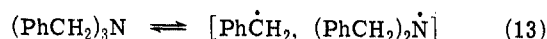
Disproportionation of benzyl radicals and dibenzylamino radicals can also be examined directly from the photolysis of *N,N,N*-tribenzylamine (Table VII). If radicals formed in the homolysis of tribenzylamine were randomly distributed in solution, the probability of encounter of a benzyl radical with another benzyl radical is one-half that with an amino radical. The low yields of bibenzyl, however, suggest that the rad-

TABLE VII
PHOTOLYSIS OF *N,N,N*-TRIBENZYLAMINE

Amine ^a			Product, mmol				
Start ^e	Recover	Solvent	PhCH ₃	(Ph-CH ₂) ₂	Ph-NCH ₂ -Ph	Ph-CHO ^d	Ph-(CH ₂) ₂ -NH
1.76 ^c	0.73	<i>c</i> -C ₆ H ₁₂	0.78	0.08	0.75	0.80	0.26
4.65 ^b		<i>c</i> -C ₆ H ₁₂	0.65	0.09	0.65		0.22
1.76 ^c	0.71	CH ₂ CN	0.66		0.80	0.74	0.21
1.75 ^c	0.86	CH ₂ CN	0.66	0.09	0.70	0.76	0.21

^a Millimoles. ^b Photolysis time, 200 min. ^c Photolysis time, 400 min. ^d Only after acid hydrolysis. ^e In 10 ml of solvent.

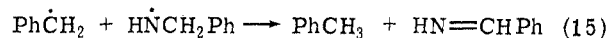
icals are not distributed statistically (provided there is no or little selectivity in the combination processes). A cage mechanism (eq 14) offers the most reasonable



explanation for the high yields of toluene and *N*-benzylbenzaldimine generated by the cross-disproportionation of benzyl and dibenzylamino radicals.

This mechanism is consistent with that proposed for the secondary steps in the photodecomposition of dibenzylamine. A major difference between them, however, lies in the idea that the two radicals are produced directly by this photochemical process, with the consequence that the initial distance of separation is probably less than that for the same pair of radicals derived from the photolysis of dibenzylamine. This difference is reflected in a higher ratio of toluene relative to bibenzyl (about 10). A value this large in the photolysis of dibenzylamine is only attained in highly viscous media.

Factors involved in the disproportionation of benzylamino radicals are also noteworthy. The mechanism presented in eq 11 does not explicitly include the cross-disproportionation of the benzyl radical and the benzylamino radical (eq 15).⁴⁴ On the other hand, the dis-



proportionation of benzyl and dibenzylamino radicals is the principal process (eq 14b) in the photolysis of *N,N,N*-tribenzylamine and other tertiary benzylamines.⁴⁵ Similarly, the photolyses of a series of *N*-benzyl-*N*-alkylamines show no evidence of disproportionation of the benzyl and alkylamino radical pair. Furthermore, the quantum yields in the photolysis of *N*-benzyl-*N*-*tert*-butylamine (and benzylamine itself) is not significantly different from that of the other alkyl analogs,⁴⁵ despite the impossibility of cross-disproportionation. Apparently, the cross-disproportionation of the secondary dialkylamino radicals occurs readily, whereas that of the primary analogs does not.

There are several explanations for this selectivity. The cross disproportionations of benzyl and alkylamino radicals generally show high selectivity,⁴⁵ and

(44) Due to the instability of benzaldimine under reaction conditions, however, we cannot rigorously establish that cage disproportionation of this radical pair does not occur at all. Some of the results presented earlier may be attributed to contribution from such a disproportionation.

(45) M. A. Ratcliff and J. K. Kochi, *Tetrahedron*, in press.

a large degree of hydrogen transfer is indicated in the transition state. Accordingly, the low stability⁴⁶ of simple alkylidene imines (eq 15) relative to their *N*-alkyl analogs would discourage cross-disproportionation with the relatively unreactive benzyl radical. Finally, the facile hydrogen transfer from the *N*-H available in secondary amines would promote the competitive scavenging of the reactive alkylamino radicals over that of the more stable dialkylamino analogs.⁴⁷

Experimental Section

All products were determined as previously described.¹⁹ Solvents used in the photolyses were, when available, commercial Spectrograde solvents used without further purification. Other hydrocarbon solvents were purified for photolysis by passing them through a 10% silver nitrate on acid-washed alumina column.⁴⁸ Nujol (Plough, Inc.) was heated to 175° (1 mm) in a vacuum oven for 20 hr. It was then diluted with 4 equiv of pentane and passed through an alumina column as described above. The pentane was removed by rotary evaporation. Solvents purified by these methods showed absorbances of less than 0.05 in a 1-cm cell. Cyclohexene was prepared by the standard method of dehydrating cyclohexanol with H₂SO₄. Commercial cyclohexene contained impurities which absorbed strongly at 250 nm. A variety of methods to purify the commercial material failed. Prepared in this manner the cyclohexene had an absorbance of 0.1 in a 1-cm cell at 250 nm. All operations were carried out with syringes using degassed and capped vessels. Isopropyl ether was stirred vigorously with an aqueous ferrous solution for 2 hr. The ether layer was dried and distilled from lithium aluminum hydride into a second flask containing more lithium aluminum hydride. A nitrogen atmosphere was maintained throughout all operations. The ether after fractionation was kept in a sealed flask. Standard solutions of both cyclohexene and isopropyl ether in cyclohexane were prepared using degassed solutions and surgical syringes. Standard solutions of amine were prepared from these stock solutions for quantum yield studies.

Dibenzylamine was purified by methods previously described.¹ At 253 nm, dibenzylamine has ϵ 357, whereas *N*-benzylbenzaldimine has ϵ 18,000. To ensure 99% absorption of the incident light by the amine the molar ratio of the amine to the imine

must be approximately 5000. This condition was easily met by both procedures used for purification, as previously described.¹

Quantum Yield Measurements.—Aliquots (3.0 ml) of standard solutions were transferred to 10 × 1 cm quartz tubes and degassed with a stream of nitrogen. For the more volatile solvents, the solutions were degassed in volumetric flasks sealed with rubber septa. After degassing, additional solvent, previously degassed, was added *via* a surgical syringe to compensate for solvent lost. Samples (3 ml) were then added to previously degassed and capped photolysis tubes with a surgical syringe.

The solutions were photolyzed in a precision merry-go-round apparatus (F. G. Moses, Co., Wilmington, Del.). A coiled low-pressure Hg lamp (Mr. Charles Shott, University of Alberta), operating at 100 mA from a 5000-V transformer, was placed in the center of the apparatus and the samples were rotated around it. A shutter allowed the system to be used only after the lamp was warmed up. A constant temperature of 32° was maintained in the reactor by the lamp.

Actinometry was carried out with chloroacetic acid using a value of 0.370 as the quantum yield for chloride formation at 32°.⁴⁹ The intensity of the lamp was found to be $7.22 \pm 0.08 \times 10^{-5}$ einstein hr⁻¹ by this method. This value was obtained by averaging 20 separate runs. The consistency was a demonstration of the uniformity of the quartz tubes and the reproducibility of the merry-go-round method.

The quantum yields reported for the dibenzylamine photolysis were measured for reactions photolyzed to less than 0.1% conversion. This limitation was necessary to ensure against filtering from the *N*-benzylbenzaldimine formed during the reaction. For two cases (0.1 and 1.0 *M*) the quantum yield was obtained from the slope of a yield *vs.* time plot which was linear over the time period involved. Other values were obtained by averaging five runs carried out simultaneously.

Viscosities were determined at $32.0 \pm 0.05^\circ$ in modified Cannon-Fenske routine viscometers calibrated by the Cannon Instrument Co., State College, Pa. Densities were obtained from literature values⁵⁰ or by direct weighing.

Registry No.—Dibenzylamine, 103-49-1; tribenzylamine, 620-40-6; benzylamine, 100-46-9; cyclohexene, 110-83-8; diisopropyl ether, 108-20-3; toluene, 108-88-3; bibenzyl, 103-29-7.

Acknowledgment.—We wish to thank the National Science Foundation, The Petroleum Research Fund of the American Chemical Society, and the U. S. Army Edgewood Arsenal for financial support of this research.

(46) P. A. S. Smith, "Open Chain Nitrogen Compounds," Vol. I, W. A. Benjamin, New York, N. Y., 1965, p 301.

(47) The reactivity sequence is H₂Ṅ > R₂Ṅ: B. G. Gowenlock and D. R. Snelling, *Advan. Chem. Ser.*, **No. 36**, 150 (1962).

(48) E. C. Murray and R. N. Keller, *J. Org. Chem.*, **34**, 2234 (1969).

(49) R. N. Smith, P. A. Leighton, and W. G. Leighton, *J. Amer. Chem. Soc.*, **61**, 2299 (1939).

(50) R. R. Breisback, *Advan. Chem. Ser.*, **No. 15** (1955); **No. 22** (1959).