10.52; mol wt, 266.3. Found: C, 59.23; H, 6.79; N, 10.64; mol wt, 261 (C_6H_6), *m/e* 266. The same product was obtained by treating the pyrrolizinone **8** with glycine ethyl ester, in the condition described below for **10, 10′a**.

The above ether extract was evaporated to dryness, yielding an oil whose physical properties and elemental analysis indicated that it was crude AcA-pro-gly-OEt (4.0 g, 60%). Upon treatment with hydroxylamine hydrochloride[1] it yielded L-prolylglycine ethyl ester hydrochloride, identical with an authentic specimen.[16]

A sample of **10, 10′** was treated with hydroxylamine, under the same conditions;[1] chromatography showed the release of glycine ethyl ester hydrochloride and of a derivative, giving a strong blue spot with iron chloride, identical with the one obtained by mixing equimolecular quantities of **8** and hydroxylamine hydrochloride.[9f,10b]

Several other reactions of AcA-proline with glycine ethyl ester and DCCI were run using different solvents (acetonitrile alone, dioxane, $CDCl_3$); work-up always gave mixtures of **10, 10′** and AcA-prolylglycine ethyl ester.

2-(α-1-Ethoxycarbonyl-1-ethylamino)ethylidene-1,3-dioxopyrrolizidine (10, 10′a, R = $CHCH_3COOC_2H_5$).—A sample of **8** as the sodium salt (812 mg, 0.004 mol), suspended in ethanol (20 ml), was treated with L-alanine ethyl ester hydrochloride (615 mg, 0.004 mol), refluxed for 1 hr, and filtered. The solution was taken to dryness and the residue was redissolved in ethyl acetate. The solution was washed with water, 1 *N* hydrochloric acid, and water, dried on sodium sulfate, and concentrated to dryness as an oil (0.54 g, 49%): uv max 306 nm (ε 20,000); [α] +30.5 (*c* 2.2); nmr δ 1.3 (t, CH_2CH_3), 1.6 (d, CH_3), 1.7–2.3 (m, CH_2CH_2), 2.50, 2.52 (=CCH_3), 2.9–3.4 (m, C_{7a} H), 3.4–3.9 (m, CH_2N), 4.0–4.6 (m, OCH_2, C_α H), 10.8 (d), 11.1 (d, NH). *Anal.* Calcd for $C_{14}H_{20}N_2O_4$: C, 59.98; H, 7.19; N, 9.99. Found: C, 59.81; H, 6.95; N, 9.61.

Registry No.—**2a**, 35211-90-6; **2b**, 35191-59-4; **2c**, 35141-03-8; **6a**, 35141-04-9; **6b**, 35141-05-0; **6c**, 35141-06-1; **8**, 2113-85-1; **10** (R = $CH_2CO_2C_2H_5$), 35191-60-7; **10′** (R = $CH_2CO_2C_2H_5$), 35141-08-3; **10** (R = $CHCH_3CO_2C_2H_5$), 35141-09-4; **10′** (R = $CHCH_3CO_2C_2H_5$), 35191-61-8; *N*-acetoacetyl-*N*-methylvaline benzylamide, 35191-62-9; *N*-benzyloxycarbonyl-*N*-methylvaline benzylamide, 35191-63-0; *N*-acetoacetyl-*N*-methylvalylglycine ethyl ester, 35191-64-1; *N*-acetoacetyl-*N*-methylvalyl-L-valine methyl ester, 35141-10-7; *N*-acetoacetylprolylurea, 35191-67-4.

Acknowledgments.—We are indebted to Dr. Mario Acampora for discussions concerning the nmr spectra and to Mr. Adriano Mencini for technical assistance.

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Photolysis of Dibenzylamine. Formation of Benzylamino and Dibenzylamino Radicals

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Direct irradiation of *N,N*-dibenzylamine in solution at 254 nm leads to efficient homolysis of the benzyl-nitrogen bond. Product studies show that the subsequent dark reactions observed are primarily those of the *N*-benzylamino radical with dibenzylamine to afford benzylamine and the dibenzylamino radical by abstraction from the N–H bond. There is no evidence for the intermediacy of the isomeric carbon-centered radical. Combination and disproportionation reactions of the benzylamino and the dibenzylamino radicals are discussed.

Early photochemical studies of nitrogen-containing systems primarily involved decomposition of ammonia[1] and simple alkylamines[2] in the gas phase. Primary and secondary alkylamines were shown to decompose by a homogeneous cleavage of the N–H bond when subjected to light from a mercury arc lamp.[3,4] Only with tertiary amines, in which no N–H bond was available, did alkyl–nitrogen homolysis become important. The photolysis of a series of primary and secondary methylamines at 77°K afforded esr spectra, which were attributed to nitrogen-centered radicals.[5]

Studies with both *n*-amylamine and *n*-butylamine showed that no decomposition corresponding to a Norrish type II reaction was associated with the photolysis of simple alkylamines.[6a] Extensive polymer formation and product arising from other than simple radical processes have obscured the elucidation of the mechanistic details of the gas-phase reactions. The solution photochemistry of amines subsequently showed that the products initially formed, when both primary and secondary amines were photolyzed in hydrocarbon media, were similar to those formed in the gas phase.[6b,7] Ammonia, always present as a secondary reaction product in photolyses carried out in the vapor phase, however, was shown to be absent in solution.[8,9]

Kinetic studies[10] involving the attack of alkyl radicals

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[1] (a) E. Warburg, *Sitzungsber. Preuss. Akad. Wiss.*, 746 (1911); *Chem. Abstr.*, **6**, 20 (1912). (b) E. Warburg, *Sitzungsber. Preuss. Akad. Wiss.*, 216 (1912); *Chem. Abstr.*, **6**, 3356 (1912). (c) W. Kuhn, *C. R. Acad. Sci.*, **177**, 956 (1923); *Chem. Abstr.*, **18**, 789 (1924). (d) W. Kuhn, *C. R. Acad. Sci.*, **178**, 708 (1924); *Chem. Abstr.*, **8**, 1787 (1924). (e) W. Kuhn, *J. Chim. Phys.*, **23**, 521 (1926); *Chem. Abstr.*, **20**, 3646 (1926). (f) J. R. Bates and H. S. Taylor, *J. Amer. Chem. Soc.*, **49**, 2438 (1927). (g) W. E. Groth, U. Schurath, and R. N. Schindler, *J. Phys. Chem.*, **72**, 3914 (1968).

[2] (a) H. J. Emeleus and H. S. Taylor, *J. Amer. Chem. Soc.*, **53**, 3370 (1931); (b) H. J. Emeleus and L. J. Jolley, *J. Chem. Soc.*, 1612 (1935).

[3] C. H. Bamford, *J. Chem. Soc.*, 17 (1939).

[4] J. V. Michael and W. A. Noyes, Jr., *J. Amer. Chem. Soc.*, **85**, 1228 (1963).

[5] S. G. Hadley and D. H. Volman, *ibid.*, **89**, 1053 (1967). See also T. Richerzhagen and D. H. Volman, *ibid.*, **93**, 2062 (1971).

[6] (a) C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1504 (1935); (b) G. H. Booth and R. G. W. Norrish, *ibid.*, 188 (1952).

[7] For other photochemical reactions of amines see (a) J. A. Barltrop and R. J. Owers, *Chem. Commun.*, 1462 (1970); (b) D. R. G. Brimage and R. S. Davidson, *ibid.*, 1385 (1971); (c) C. H. Niu and V. I. Stenberg, *ibid.*, 1430 (1971); (d) D. Bryce-Smith, M. T. Clarke, A. Gilbert, G. Klunkin, and G. Manning, *ibid.*, 916 (1971); (e) N. Paillous and A. Lattes, *Tetrahedron Lett.*, 4945 (1971).

[8] The photolysis of both di- and triethylamine has been carried out on the neat liquids with a medium-pressure mercury lamp.[9] Due to the long periods of irradiation (90 hr) and the consequent complexity of the resulting products, mechanistic arguments should be considered tenuous.[9a]

[9] (a) L. T. Allan and G. A. Swan, *J. Chem. Soc.*, 4822 (1965); (b) C. H. Niu and V. I. Stenberg, *Chem. Commun.*, 1430 (1971).

[10] (a) P. J. Kozak and H. Gesser, *J. Chem. Soc.*, 448 (1960); (b) R. K. Brinton, *Can. J. Chem.*, **38**, 1339 (1960); (c) P. Gray and J. C. J. Thynne, *Trans. Faraday Soc.*, **59**, 2275 (1963); (d) P. Gray and A. Jones, *ibid.*, **62**, 112 (1966); (e) P. Gray, A. Jones, and J. C. J. Thynne, *ibid.*, **61**, 474 (1965); (f) D. A. Edwards, J. A. Kerr, A. C. Lloyd, and A. F. Trotman-Dickerson, *J. Chem. Soc. A*, 1500 (1966).

on various alkylamines, and the determination of bond dissociation energies of amines,[11] have contributed to an understanding of the chemistry of nitrogen-centered radicals. The heats of formation of amino radicals generally decrease with alkyl substitution in the order $\dot{N}H_2 > CH_3\dot{N}H > (CH_3)_2\dot{N}$ [that is, $\Delta H_f = 47.2, 45.2$, and 38.2 kcal mol^{-1}, respectively].[12] Thus, the stability of radicals centered on nitrogen exhibits the same trend as those of the carbon analogs.

Most of our knowledge of the reactions of the nitrogen-centered radicals has come from the dimethylamino radical generated thermally or photochemically from tetramethyltetrazene.[13,14] This radical is reported to abstract the α hydrogen atom from cumene (as evidenced by the formation of dimethylamine and bicumyl)[15] and add to α-methylstyrene.[16] The photolysis of *N*-(*tert*-butyl)-*N*-chloroacetamide in benzene afforded the amido radical, which failed to add to any of a series of olefins.[17] It was concluded that neutral amino, alkylamino, or acylamino radicals abstract hydrogen from olefins in preference to addition to the double bond. The possible exceptions to this generalization are protonated amino radicals. The previously observed addition to α-methylstyrene[16] may be an abstraction reaction followed by radical combination. Support for this view was provided by the fact that no addition products were formed when the dimethylamino radical was produced in the presence of stilbene.[18] However, the addition of the dimethylamino radical to ethylene in a vapor phase process has been reported.[19] Mackay and Waters[20] generated the dimethylamino radical photochemically from the tetrazene in the presence of hydrogen donors and concluded that hydrogen abstraction by a nitrogen-centered radical is a very selective process and occurs only when a relatively stable radical results.

In light of the divergent data surrounding amino radicals, we have investigated the photochemical decomposition of *N*,*N*-dibenzylamine as a system for the production of amino radicals.

Results and Discussion

Dibenzylamine decomposed to a mixture of products when irradiated with 253-nm light. Hydrogen, found to be a major product in the photolysis of primary and secondary aliphatic amines[3] in the gas phase, was not detected in solution.[21] We find that the major products included toluene, benzylamine, and *N*-benzylbenzaldimine. Tribenzylamine and bibenzyl are formed in lesser quantities but of equal importance for mechanistic considerations. Table I lists the compounds identified from the photolysis carried out in several solvents. These product studies are based on reactions allowed to proceed to only ~10% completion, thus avoiding complications due to secondary photolysis of the initially formed products. The presence of bibenzyl, toluene, and benzylamine suggests an initial C–N bond homolysis (eq 1) from which

TABLE I
PRODUCTS FROM THE PHOTOLYSIS OF DIBENZYLAMINE AT 253 nm[a]

	Product, mmol				
Concn, *M*	$PhCH_3$	$PhCH_2NH_2$	$PhCH{=}NCH_2Ph$	$(PhCH_2)_3N$	$(PhCH_2)_2$
0.02[b]	0.04	0.05	0.03	0.002	0.01
0.15[c]	0.06	0.06	0.09	0.02	0.02
0.20[c]	0.10	0.07	0.10	0.02	0.02
0.25[c]	0.11	0.09	0.11	0.03	0.02
0.50[c]	0.14	0.13	0.12	0.05	0.02
0.75[c]	0.16	0.16	0.15	0.07	0.02
1.00[c]	0.165	0.19	0.16	0.08	0.02
1.50[c]	0.19	0.23	0.17	0.10	0.02
0.25[d]	0.09	0.07	0.09	0.04	0.027
0.50[d]	0.11	0.11	0.11	0.06	0.030
0.75[d]	0.12	0.12	0.12	0.07	0.035
1.00[d]	0.13	0.14	0.14	0.10	0.035
1.50[d]	0.14	0.16	0.15	0.12	0.33
0.5[e]	0.06	0.04	0.07	0.02	0.01
1.0[e]	0.07	0.05	0.09	0.03	0.01

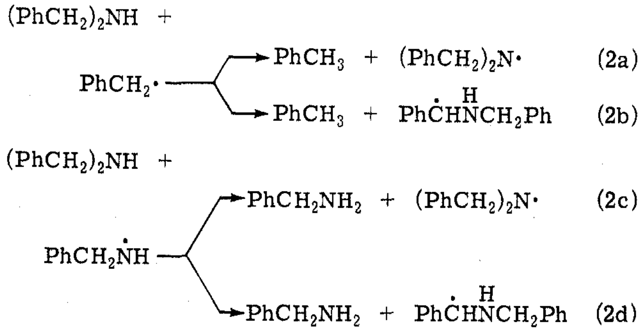
[a] Photolysis for 60 min. [b] Pentane. [c] Cyclohexane. [d] Acetonitrile. [e] Methanol.

$$(PhCH_2)_2NH \xrightarrow{h\nu} PhCH_2\cdot + PhCH_2\dot{N}H \qquad (1)$$

both toluene and benzylamine could result by subsequent hydrogen abstraction.

Both cyclohexene and bicyclohexyl are products from the bimolecular reaction of two cyclohexyl radicals. The absence of detectable amounts of these compounds indicates that attack on this solvent is minor and that the products arise predominantly by reaction with substrate. The benzyl radical is not expected to attack cyclohexane to any significant extent at room temperature and our observation that the benzylamino radical does not dehydrogenate cyclohexane is in general agreement with the MacKay and Waters[20] studies with the dimethylamino radical. Similarly, the absence of succinonitrile precludes appreciable attack at the α hydrogens of acetonitrile.

If attack on the substrate is considered to be the primary process, four reactions involving the abstraction of hydrogen from dibenzylamine are possible



$$(PhCH_2)_2NH + PhCH_2\cdot \longrightarrow PhCH_3 + (PhCH_2)_2N\cdot \qquad (2a)$$

$$\longrightarrow PhCH_3 + Ph\dot{C}H\overset{H}{N}CH_2Ph \qquad (2b)$$

$$(PhCH_2)_2NH + PhCH_2\dot{N}H \longrightarrow PhCH_2NH_2 + (PhCH_2)_2N\cdot \qquad (2c)$$

$$\longrightarrow PhCH_2NH_2 + Ph\dot{C}H\overset{H}{N}CH_2Ph \qquad (2d)$$

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(11) (a) M. Szwarc, *Proc. Roy. Soc., Ser. A*, **198**, 285 (1949); (b) M. Szwarc, *ibid.*, **197**, 267 (1949); (c) J. A. Kerr, R. C. Serhar, and A. F. Trotman-Dickerson, *J. Chem. Soc.*, 3217 (1963); (d) B. G. Gowenlock, P. P. Jones, and J. R. Majer, *Trans. Faraday Soc.*, **57**, 23 (1961); (e) N. J. Friswell and B. G. Gowenlock, *Advan. Free Radical Chem.*, **2**, 7 (1967).

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(15) B. L. Erusalimsky, B. A., Dolgoplosk, and A. P. Kavuneneko, *Zh. Obshch. Khim.*, **27**, 257 (1957).

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

(17) R. S. Neale, N. L. Marcus and R. G. Schepers, *J. Amer. Chem. Soc.*, **88**, 3051 (1966). See also R. S. Neale, *Synthesis*, **1** (1971); P. Kovacic, M. K. Lowery, and S. W. Horgan, *Chem. Res.*, **70**, 639 (1970).

(18) R. E. Jacobson, K. M. Johnston, and G. H. Williams, *Chem. Ind. (London)*, 157 (1967).

(19) A. Good and J. C. J. Thynne, *J. Chem. Soc. B*, 684 (1967).

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

(21) It has recently been suggested,[14a] however, that dimethylamino radicals generated photochemically from tetramethylurea or dimethylacetamide afford hydrogen by disproportionation.

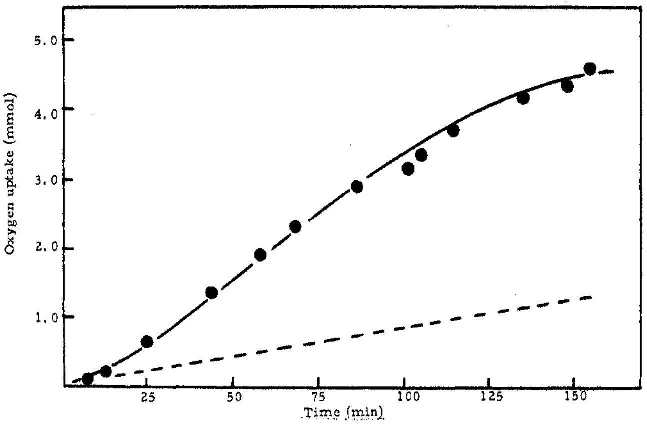


Figure 1.—Oxygen uptake in thermal decomposition of dicumyl peroxide in dibenzylamine: (●) experimental; (---) theoretical uptake assuming no chain reaction (125°).

(eq 2). Several results indicate that attack is mainly at the N–H bond. Since there are no authenticated examples of 1,2-hydrogen shifts[22] (eq 3), the formation

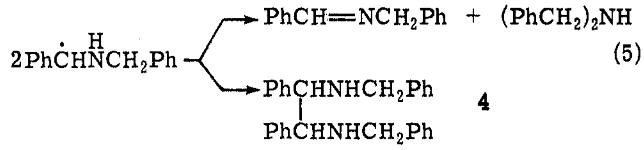
$$\underset{\mathbf{2}}{\mathrm{Ph\dot{C}HNCH_2Ph}} \not\longrightarrow \underset{\mathbf{1}}{\mathrm{PhCH_2\dot{N}CH_2Ph}} \qquad (3)$$

of tribenzylamine is best explained as a dimerization process involving a benzyl radical and a dibenzylamino radical formed in either step 2a or 2c.

Tribenzylamine was identified (after separation by preparative vpc) by its pmr spectrum and it mass spectral fragmentation pattern when compared with authentic tribenzylamine. The mass spectrum of tribenzylamine shows a molecular ion at *m/e* 287, an M − 1 peak at *m/e* 286, and major peaks at *m/e* 196 [$(PhCH_2)_2N^+$], 210 [$(PhCH_2)_2NCH_2^+$], and 91 [$PhCH_2^+$]. The isomer $PhCH_2CH(Ph)NHCH_2Ph$ (**3**), which would be expected from the dimerization of the carbon-centered radical **2** and a benzyl radical, has a completely different fragmentation pattern. Neither a molecular ion nor an M − 1 peak is observed in **3**, and the most prominent ion is at *m/e* 106 ($PhCH_2NH^+$).

The chemistry of the carbon-centered radical **2** was further studied by examining the reaction of dibenzylamine with alkoxy radicals, which were generated thermally from both di-*tert*-butyl and dicumyl peroxide (eq 4 and 5). The carbon–carbon dimer **4** and

$$\mathrm{RO\cdot} + \mathrm{(PhCH_2)_2NH} \longrightarrow \mathrm{ROH} + \mathrm{Ph\dot{C}H\overset{H}{N}CH_2Ph} \qquad (4)$$



$$2\,\mathrm{Ph\dot{C}H\overset{H}{N}CH_2Ph} \longrightarrow \begin{cases} \mathrm{PhCH{=}NCH_2Ph} + \mathrm{(PhCH_2)_2NH} \\ \begin{array}{l} \mathrm{PhCHNHCH_2Ph} \\ \quad | \\ \mathrm{PhCHNHCH_2Ph} \end{array} \quad \mathbf{4} \end{cases} \qquad (5)$$

N-benzylbenzaldimine are the predominant products, as shown in Table II. It is apparent that alkoxy attack occurred predominantly at carbon[23] to produce radical **2**, since the results differ from those observed with the *N,N*-dibenzylamino radical derived from the decomposition of tetrabenzyltetrazene (*vide infra*). The absence of toluene and bibenzyl indicates that β scission (eq 6) is not important for the radical **2**. The oxy-

$$\mathrm{Ph\dot{C}\overset{H}{H}NCH_2Ph} \longrightarrow \mathrm{PhCH{=}NH} + \mathrm{PhCH_2\cdot} \qquad (6)$$

gen analog of **2**, however, generated in dibenzyl ether is known to cleave directly to benzaldehyde and a benzyl radical.[24]

TABLE II

REACTION OF DIALKYL PEROXIDES AND DIBENZYLAMINE[a]

Peroxide		Product, mmol				
R	mmol	Alcohol[e]	Ketone[f]	$PhCH{=}NCH_2Ph$	Dimer **4**	PhCHO
tert-Butyl[b]	1.4	2.12		0.51	0.59	
Cumyl[c]	1.04	2.0		0.60	0.35	0.59[d]
Cumyl	1.12	2.20	0.2	0.65	0.24	
Cumyl	3.5	6.5	0.5	2.2	1.0	

[a] Run in 15 ml of neat amine at 130° for 6 hr (degassed with N_2). [b] Di-*tert*-butyl peroxide. [c] Dicumyl peroxide. [d] Only after acid hydrolysis. [e] Either *tert*-butyl alcohol or cumyl alcohol. [f] Either acetone or acetophenone.

When oxygen was introduced into the system, the yield of dimer dropped below detectable limits, and the imine yield increased well beyond the stoichiometric limit imposed by the peroxide (Table III).

TABLE III

EFFECT OF OXYGEN ON PEROXIDE REACTIONS WITH DIBENZYLAMINE[a]

		Product, mmol				
Dicumyl peroxide	O_2	Ph-$C(CH_3)_2$-OH	$PhC(=O)CH_3$	$PhCH{=}NCH_2Ph$	PhCHO *d*	PhCHO *e*
1.10	*b,f*	2.1	0.1	3.95		
1.10	7.0[c,g]	1.91	0.23	5.73	2.3	8.0
1.10	5.5[c,h]	1.80	0.4	4.6	1.9	6.6

[a] Same conditions as previously described, except that oxygen was present. [b] Run under 20 psi oxygen. [c] Oxygen uptake followed manometrically. [d] Yield before hydrolysis. [e] Yield after hydrolysis. [f] Run 360 min. [g] Run 250 min. [h] Run 150 min.

Autoxidation of the amine was not evident in the absence of peroxide. The difference in the yield of benzaldehyde before and after hydrolysis was identical with the amount of imine present and indicates that no other aldehyde precursor was formed (*e.g.*, PhCH=NH). The effect of oxygen can be interpreted as trapping the radical **2** to produce an intermediate peroxy radical **5**, which is known to undergo a wide

$$\underset{\mathbf{2}}{\mathrm{Ph\dot{C}\overset{H}{N}CH_2Ph}} + O_2 \longrightarrow \underset{\mathbf{5}}{\mathrm{Ph\overset{\cdot OO}{C}H\overset{H}{N}CH_2Ph}} \qquad (7)$$

variety of reactions.[25] Further mechanistic details of the reaction were not investigated, although, as Figure 1 indicates, some radical chain process occurs in which the peroxy radical **5** could be a possible intermediate. Alternatively, the intermediacy of a nitroxide moiety in a mechanism similar to that suggested by DeLaMare[26] to explain the oxidation of dibenzyl-

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[22] O. L. Chapman, "Organic Photochemistry," Vol. I, Marcel Dekker, New York, N. Y., 1967.

[23] E. S. Huyser, C. J. Bredeweg, and R. M. Van Scoy, *J. Amer. Chem. Soc.*, **86**, 4148 (1964).

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[25] G. A. Russell, "Peroxide Reaction Mechanisms," J. Edwards, Ed., Interscience, New York, N. Y., 1962.

[26] (a) H. E. DeLaMare, *J. Org. Chem.*, **25**, 2114 (1960); (b) G. M. Coppinger and J. D. Swalen, *J. Amer. Chem. Soc.*, **83**, 4900 (1961).

amine to the imine by *tert*-butyl hydroperoxide is possible.

The presence of the dimer **4** in the peroxide reaction (eq 4, 5) indicates that both combination and disproportionation reactions between two carbon-centered radicals **2** does occur. The absence of such dimers in the photochemical reaction further rules out the involvement of radical **2** to any significant degree in that reaction.

An independent source for the dibenzylamino radical **1** was sought, and *N*,*N*,*N'*,*N'*-tetrabenzylhydrazine (**6**) was first used, since this compound was expected to decompose photochemically to a pair of dibenzylamino radicals. Table IV lists the yields of the products identified from the photolysis of **6**. The high yield of toluene and the absence of dibenzylamine, however, indicates that C–N bond cleavage occurs rather than a process to produce the desired radical **1**. This reaction was not studied further, since radical **1** could be generated from tetrabenzyltetrazene **7**. The photolysis was carried out at 310 nm, which represents the tail of the tetrazene band having a maximum at 290 nm (ϵ 1.15 × 10^4). At this wavelength all of the products are optically transparent and nitrogen is liberated quantitatively. The yield of dibenzylamine was approximately 30% greater than the yield of the imine, as shown in Table V. The results are consistent with the general scheme shown below, although some attack on the solvent is indicated.[27]

TABLE IV

PHOTOLYSIS OF TETRABENZYLHYDRAZINE AT 253 nm[a]

Hydrazine[b] Start	Hydrazine[b] End	Product, mmol $PhCH_3$	Product, mmol $(PhCH_2)_2$	Product, mmol $PhCHO$[c]	Product, mmol $(PhCH_2)_2$-NH	Product, mmol PhCH=NCH$_2$Ph
0.38	t	0.30	0.14	~0.1	t	t

[a] Photolysis time, 320 min. [b] In cyclohexane (mmol). [c] Only after acid hydrolysis. t = trace (<0.01 mmol).

TABLE V

PHOTOLYSIS OF TETRABENZYLTETRAZENE AT 310 nm[a]

Tetrazene,[b] mmol	Product, mmol N_2	Product, mmol $(PhCH_2)_2NH$	Product, mmol PhCH=NCH$_2$Ph	$\frac{\Sigma N \text{ compd}}{2N_2}$
0.24	0.236	0.29	0.21	1.07
0.24	0.27	0.27	0.18	0.84
0.48	0.465	0.58	0.38	1.03

[a] Pyrex filter. [b] In 10 ml of cyclohexane.

$$\underset{\mathbf{7}}{\mathrm{(PhCH_2)_2NN{=}NN(CH_2Ph)_2}} \xrightarrow{h\nu} \mathrm{N_2} + 2\mathrm{(PhCH_2)_2N\cdot} \quad (8)$$

$$\underset{\mathbf{1}}{2\mathrm{(PhCH_2)_2N\cdot}} \longrightarrow \mathrm{(PhCH_2)_2NH} + \mathrm{PhCH{=}NCH_2Ph} \quad (9)$$

$$\mathbf{1} \not\longrightarrow \underset{\mathbf{6}}{\mathrm{(PhCH_2)_2NN(CH_2Ph)_2}}$$

The reaction between the two dibenzylamino radicals represented in eq 9 is interesting, since the absence of the hydrazine dimer **6** implies that the radical **1** only undergoes disproportionation to the exclusion of dimerization.[28] A 1,2-hydrogen shift from carbon to nitrogen is also ruled out,[22] since it would produce radical **2** and subsequently the dimer **4**. It thus appears that any reaction leading to the nitrogen-centered radical **1** will result in disproportionation to the exclusion of dimerization, whereas carbon-centered radicals afford dimers as well as disproportionation products.[30]

Since the involvement of the carbon-centered radical **2** can be ruled out, two alternative reactions, 2a and 2c, remain. To evaluate the importance of reaction 2a, *N*-deuteriodibenzylamine was photolyzed and the toluene was isolated by preparative gas chromatography (see Experimental Section). The pmr spectrum of the toluene obtained in this manner showed a relative intensity of the aromatic to methyl protons in a ratio of 5.0 to 3.0. The absence of labeled toluene thus eliminates reaction 2a and leaves 2c as the most likely process occurring in the dark, subsequent to homolysis.[31]

$$\mathrm{(PhCH_2)_2ND} + \mathrm{PhCH_2\cdot} \not\longrightarrow \mathrm{PhCH_2D} + \mathrm{(PhCH_2)_2\dot{N}}$$

Although bibenzyl was formed in the photolysis of dibenzylamine and almost certainly results from a radical combination reaction, the corresponding dimer *N*,*N*-dibenzylhydrazine **8** from the benzylamino radical was not detected. This observation further strengthens the argument favoring reaction 2c as the major dark reaction, since such an abstraction process would remove the benzylamino radical and thereby prevent its dimerization. *sym*-Dibenzylhydrazine **8** is the expected product if hydrogen abstraction leading to benzylamine were not efficient. The stability of **8** under the reaction conditions was established (see Experimental Section).

The formation of both the imine and tribenzylamine could arise by the following series of reactions (eq 10).

$$\mathrm{PhCH_2\cdot} + \mathrm{(PhCH_2)_2N\cdot} \begin{cases} \longrightarrow \mathrm{(PhCH_2)_3N} & (10a) \\ \longrightarrow \mathrm{PhCH_3} + \mathrm{PhCH{=}NCH_2Ph} & (10b) \end{cases}$$

$$2\,\mathrm{(PhCH_2)_2N\cdot} \longrightarrow \mathrm{(PhCH_2)_2NH} + \mathrm{PhCH{=}NCH_2Ph} \quad (10c)$$

The stoichiometric relationship between the imine, toluene, and benzylamine is shown in Table VI. If only reactions 2c and 10b were involved in the formation

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[27] Attack on solvent by the dibenzylamino radical under these conditions is not necessarily inconsistent with our previous conclusion regarding the absence of solvent attack during the photolysis of dibenzylamine. In the former case the dibenzylamino radical can attack solvent or undergo (cage) combination–disproportionation reactions. The relative concentrations of the solvent and radicals would permit attack on solvent even if it were energetically unfavorable. In the second case, the initially formed benzylamino radical can react with more substrate (dibenzylamine) rather than react with the solvent. To preclude attack on solvent the relative rate constants for attack on substrate should be more than ten times faster than attack on solvent.

[28] Moreover, the oxidation of dibenzylamine with nickel peroxide also led to no dimeric products.[29]

[29] K. S. Balachandran, I. Bhatnagar, and M. V. George, *J. Org. Chem.*, **33**, 3891 (1968).

[30] However, disproportionation of dimethylamino radicals to imine and hydrogen has been proposed.[14a]

[31] Benzyl radicals have been postulated to attack the N–H bond in at least one example [J. Hutton and W. A. Waters, *J. Chem. Soc.*, 4253 (1965)]. It was suggested that di-*tert*-butyl peroxide in refluxing toluene produced benzyl radicals, which attack indole by a free-radical abstraction process and ultimately afford *N*-benzylindole. In this case, however, there appears to have been no attempt to eliminate the possibility of a radical addition mechanism.

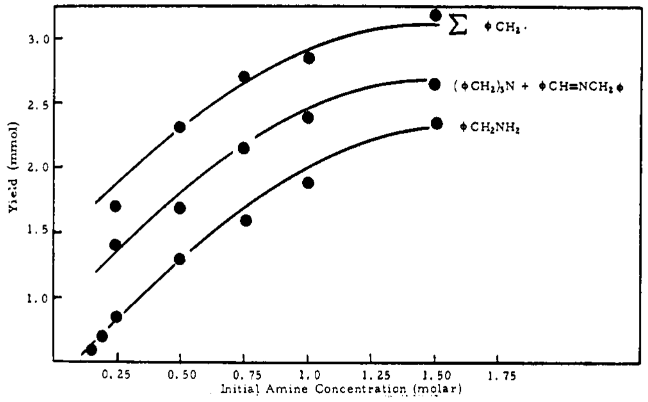


Figure 2. Stoichiometric relationship of the products formed in the photolysis of dibenzylamine: $\Sigma\phi CH_2 = \phi CH_3 + (\phi CH_2)_2 + (\phi CH_2)_3N$.

of these compounds, the ratio shown in the last column of Table VI should be 2.

TABLE VI
STOICHIOMETRY OF IMINE FORMATION

	Product, mmol				$\frac{PhCH_3 + PhCH_2NH_2}{PhCH{=}NCH_2Ph}$
$(PhCH_2)_2NH$[a]	$PhCH_3$	$PhCH_2NH_2$	$PhCH{=}NCH_2Ph$	PhCHO[b]	
0.26	0.28	0.22	0.35	0.36	1.45
0.52	0.41	0.29	0.43	0.47	1.60
1.55	0.64	0.55	0.63	0.68	1.89
2.6	0.66	0.79	0.72	0.84	2.02
3.9	0.86	0.94	0.88	0.94	2.05
5.2 (neat)	0.92	1.14	1.05	1.08	1.95

[a] Molar concentration in CH_3CN (10 ml). [b] After acid hydrolysis.

A ratio of 2 was indeed observed at higher amine conentrations. The greater yield of imine compared to toluene obtained in some cases, however, indicates that the disproportionation of two amino radicals (eq 10c) remains as a possible minor pathway. The overall stoichiometric relationship among the products of the reaction is shown in Figure 2. Although the yield of benzylamine remains below the yield of products derived from the benzyl radical, the difference is constant throughout the range of concentrations studied.[32]

The disappearance of dibenzylamine in Figure 3 is initially rapid, but is apparently inhibited by the product (imine), which has a much larger absorbance (ε 18,000) than that of the reactant (ε 357). The filtering of the light can be shown by the retardation of the rate due to the deliberate addition of imine (Figure 3) which can be recovered quantitatively. At higher conversions, the percentage increase in the concentration of the imine is no longer significant and the reaction appears to be linear. We found the imine to be completely stable under our photolytic conditions, although other workers have shown that compounds of this type undergo photochemical dimerizations, particularly in alcoholic media.[33-35]

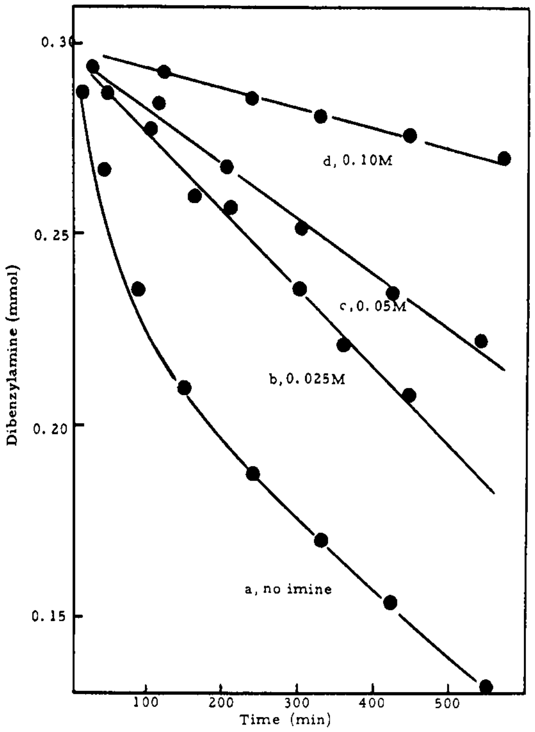
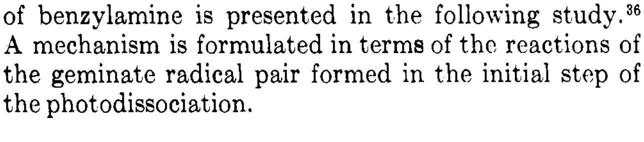


Figure 3—The effect of added N-benzylbenzaldimine on the rate of photolysis of dibenzylamine: $(\phi CH_2)_2NH$, 0.1 M; imine concentration shown.

A mechanism generally consistent with the foregoing discussion is summarized below.

$$(PhCH_2)_2NH \underset{}{\overset{h\nu}{\rightleftharpoons}} PhCH_2\cdot + PhCH_2\dot{N}H$$

$$PhCH_2\dot{N}H + (PhCH_2)_2NH \longrightarrow PhCH_2NH_2 + (PhCH_2)_2N\cdot$$



$$PhCH_2\cdot + (PhCH_2)_2N\cdot \longrightarrow PhCH_3 + PhCH{=}NCH_2Ph$$

$$PhCH_2\cdot + (PhCH_2)_2N\cdot \longrightarrow (PhCH_2)_3N$$

$$2PhCH_2\cdot \longrightarrow PhCH_2CH_2Ph$$

$$2(PhCH_2)_2N\cdot \longrightarrow (PhCH_2)_2NH + PhCH{=}NCH_2Ph$$

A study of the effects of changes in the viscosity of the medium on the quantum yield for the formation of benzylamine is presented in the following study.[36] A mechanism is formulated in terms of the reactions of the geminate radical pair formed in the initial step of the photodissociation.

Experimental Section

Dibenzylamine.—Commercial dibenzylamine was found to contain significant amounts of N-benzylbenzaldimine and lesser quantities of benzylamine. Two methods of purification were found satisfactory.

Into a 2-l. flask was place 400 ml of the amine and 400 ml of dimethoxyethane. Ten grams of sodium borohydride was added and the mixture was refluxed for 12 hr. To the slightly cooled solution was added 1 l. of a saturated solution of sodium bicar-

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[32] The absence of a complete material balance (especially at low concentrations of amine) may be due to loss of nitrogenous fragments, particularly the benzylamino radical. The cage disproportionation of benzyl and benzylamino radicals is one such possibility, but the absence of excess toluene makes it unlikely. The formation of benzaldimine was not tested directly due to its instability (cf. P. A. Smith, "Open Chain Nitrogen Compounds," Vol. I, W. A. Benjamin, New York, N. Y., 1965, p 301).

[33] A. Padwa, W. Bergmark, and D. Pashayan, J. Amer. Chem. Soc., **91**, 2653 (1969).

[34] B. Fraser-Reid, A. McLean, and E. Usherwood, Can. J. Chem., **47**, 4511 (1969).

[35] P. Beak and C. R. Payet, J. Org. Chem., **35**, 3281 (1970).

[36] M. A. Ratcliff, Jr., and J. K. Kochi, J. Org. Chem., **37**, 3275 (1972).

bonate. The mixture was then heated to 60° and stirred for 1 hr to hydrolyze the borate formed during reduction. The amine was extracted with two 500-ml portions of ether. The ether was removed by rotary evaporation and the amine was distilled at 140° (3 mm). Alternatively, the amine was dissolved in an equal volume of 95% ethanol and 1 g of 5% palladium on charcoal was added. The resulting mixture was shaken at room temperature under a hydrogen atmosphere of 50 psi for 6 hr. The palladium was removed by filtration and the alcohol was removed by rotary evaporation. The amine was distilled as before.

Both methods completely removed the imine and left only trace amounts of benzylamine as analyzed by gas chromatography.

Solvents.—Solvents used in the photolyses were, when available, commercial spectrograde solvents. These were used without further purification. Other hydrocarbon solvents were purified for photolysis by passing them through a column packed with acid-washed alumina impregnated by 10% silver nitrate.[37] All solvents used in these experiments had an absorbance of less than 0.05 in a 1-cm cell.

***N*-Deuteriodibenzylamine** $[(PhCH_2)_2ND]$.—Dibenzylamine (25 g) and 100 ml of deuterium oxide were placed in a 250-ml round-bottom flask. Three drops of concentrated sulfuric acid was added and the mixture was shaken for 3 days. The amine was extracted with ether, which was removed by rotary evaporation. This process was repeated three additional times. After the final exchange, the ether extract was thoroughly dried over sodium sulfate and filtered, and the ether was removed as before. The amine was distilled under vacuum. Proton magnetic resonance (pmr) analysis indicated the deuterium enrichment to be greater than 98%.

Benzalazine $(PhCH{=}NN{=}CHPh)$.—Benzaldehyde (100 g) was dissolved in 200 ml of benzene and placed in a round-bottom flask equipped with a Dean–Stark trap. The solution was warmed and 25 g of hydrazine hydrate was added from a dropping funnel. The water formed was removed as a benzene azeotrope. After the theoretical amount of water had been obtained the benzene was removed by rotary evaporation, leaving a yellow solid which was recrystallized from ethanol.

***sym*-Dibenzylhydrazine** $(PhCH_2NHNHCH_2Ph)$.—Benzalazine (5 g) and 1 g of platinum on calcium carbonate (5%) were placed in an hydrogenation flask and 100 ml of ethyl acetate was added. The mixture was shaken on a Parr apparatus at room temperature under 50 psi hydrogen for 8 hr. The ethyl acetate was removed by rotary evaporation and the residual oil was added to an aqueous hydrochloric acid solution. The hydrochloride was washed with methanol and ether, mp 212° dec (lit.[38] mp 215–217° dec).

Acetylhydrazide $(CH_3CONHNH_2)$.—Over a period of 1 hr, 46 g of ethyl acetate was added to a refluxing solution of 25 g of hydrazine hydrate and 15 ml of ethanol. After the addition of the ethyl acetate was completed, the mixture was refluxed for an additional 4 hr, after which time the heat was removed and the mixture was allowed to stand overnight. The ethanol and remaining ethyl acetate were removed by rotary evaporation, leaving an oil containing unreacted hydrazine hydrate and an oil which was distilled under vacuum. Water heated to 75° was pumped through the condenser to prevent solidification, and the receiver was also placed in a hot water bath for the same purpose. The fraction boiling at 134–136° (21 mm) was retained, mp 59–60° (lit.[39] mp 60°).

Tetrabenzylhydrazine $[(PhCH_2)_2NN(CH_2Ph)_2]$.—Benzyl bromide (55 g, 0.6 M) was added dropwise to a solution of 200 ml of water, 60 g of sodium carbonate monohydrate, and 15 g of acetylhydrazide heated to 60°. After the addition was completed, the mixture was refluxed for 1 hr, during which time an oily layer separated. The mixture was cooled and extracted with three 100-ml portions of ether. Removal of the ether by rotary evaporation left a white solid. The solid was taken up in a minimum amount of hot 95% ethanol and allowed to crystallize. The flat white needles which formed were collected by filtration and air dried: mp 139–139.5° (lit.[40] mp 139–140°); pmr[41] δ 3.77 (2.0) ($-CH_2-$) s, 7.10 (5.0) (aromatic) s.

***unsym*-Dibenzylhydrazine** $[(PhCH_2)_2NNH_2]$.—Hydrazine hydrate (200 g) was placed in a three-necked, round-bottom flask equipped with a magnetic stirrer. The flask was immersed in a Dry Ice–isopropyl alcohol bath, and benzyl bromide (100 g) was added from a dropping funnel at a rate such that the temperature remained below 10°. After the addition was complete, the solution was heated to 75° for 2 hr and upon cooling, extracted with benzene. The benzene was removed by rotary evaporation and the residual oil (which solidified upon cooling) was distilled under vacuum. Water heated to 75° was pumped through the condenser to prevent solidification. The collected fraction had bp 169–171° (5 mm), solidified upon cooling, and was recrystallized from a mixture of ethanol and petroleum ether (bp 30–60°): mp 64–66° (lit. mp 63–64°,[42] 65°,[43] 81–83°,[44] 54–56°[45]); pmr[41] δ 2.82 (1.0) ($-NH_2$) s, 3.80 (1.95) ($-CH_2-$) s, 7.32 (5.05) (aromatic) s.

Tetrabenzyltetrazene $[(PhCH_2)_2NN{=}NN(CH_2Ph)_2]$.—*unsym*-Dibenzylhydrazine (11 g) was placed in a 500-ml, three-necked round-bottom flask. Ethanol (200 ml) was added and the solution was degassed with a nitrogen stream. Freshly prepared mercuric oxide (21 g) was added to the solution. The mixture was then heated in an oil bath for 3 hr at a temperature which allowed the ethanol to reflux gently. After cooling, the mixture was filtered and the filtrate was heated to boiling and refiltered. Upon cooling to room temperature, long white needles formed, mp 96.5–98°. After a second recrystallization the melting point was 96.5–97° (lit. mp 99–100°,[46] 95–96°[47]): pmr[41] δ 4.36 (2.0) ($-CH_2-$) s, 7.23 (5.0) (aromatic) s (broad); uv λ_{max} 290 nm (ϵ 11,500), 215 (45,000); ir 6.7 (m), 6.9 (m), 9.4 (m), 10.5 μ (s).

Anal. Calcd for $C_{28}H_{28}N_4$: C, 80.00; H, 6.66; N, 13.33. Found: C, 79.99; H, 6.55; N, 13.56.

Product Analysis.—All quantitative analyses were performed by vapor phase chromatography (vpc) on a Varian Aerograph Model 1200 gas chromatograph equipped with a flame ionization detector. Products were identified by comparing their retention times with those of authentic samples on at least two columns whose separation characteristics differed. Quantitative analysis was performed by the internal standard method with a marker chosen, where possible, which had similar functional group characteristics and a retention time close to that of the compound being determined. Basic materials were analyzed by adding a known amount of marker to a measured portion of the reaction solution. This solution was analyzed directly by vpc.

Neutral materials and hydrolysis products (*i.e.*, benzaldehyde from the imine) were determined after acidic hydrolysis. A partition technique was used. Into a 2-dram vial was measured 1 ml of the reaction mixture, 1 ml of a standard marker solution, and 1 ml of an 8 N sulfuric acid solution. Three milliliters of ether or hexane was then added to the solution and the vial was capped. Samples were taken from the organic layer for vpc analysis. Calibrations were performed under conditions identical with those of the analysis.

Infrared spectra were obtained on a Perkin-Elmer Model 137b or Beckman IR-8 spectrometer. Pmr spectra were taken, unless otherwise specified, in deuteriochloroform on a Varian A-60A spectrometer. Chemical shifts are reported in δ units relative to tetramethylsilane as an internal standard. Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. Mass spectra were recorded on a Varian CH-7 mass spectrometer. Ultraviolet spectra were obtained with a Beckman DB-G spectrophotometer.

Analysis of *sym*-Dibenzylhydrazine.—The hydrazine, stored as the hydrochloride, was released with dilute base. For vpc

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

(38) A. F. Bickel and W. A. Waters, *Recl. Trav. Chim. Pays-Bas*, **69**, 312 (1950).

(39) A. N. Kost and R. S. Sagitullin, *Zh. Obshch. Khim.*, **27**, 3338 (1957); *Chem. Abstr.*, **52**, 9071*c* (1958).

(40) R. T. Merrow and R. van Dolah, *J. Amer. Chem. Soc.*, **76**, 4522 (1954).

(41) Proton abundance by integration are shown in parentheses and assignments are given. Abbreviations are s, singlet; d, doublet; q, quartet; and m, multiplet.

(42) A. N. Kost and R'S. Sagitullin, *Fiz. Khim.*, **14**, 225 (1959); *Chem. Abstr.*, **53**, 21894*a* (1959).

(43) G. Fedor, *Chem. Phys.*, **2**, 167 (1949); *Chem. Abstr.*, **44**, 6414*a* (1950).

(44) L. A. Carpino, *J. Amer. Chem. Soc.*, **82**, 3133 (1960).

(45) H. Fox, J. T. Gibas, and A. Motchane, *J. Org. Chem.*, **21**, 349 (1956).

(46) C. G. Overberger and B. S. Marks, *J. Amer. Chem. Soc.*, **77**, 4104 (1955).

(47) R. L. Hinman and K. L. Hamm, *ibid.*, **81**, 3294 (1959).

analysis, the hydrochloride was weighed into a 2-dram vial to which 2 ml of 3 N potassium hydroxide was added together with a known amount of marker (in acetonitrile) and 3 ml of ether. The organic layer was analyzed directly. It was found that in the presence of air the hydrazine decomposed over a period of 4 hr to unidentified products. Under nitrogen, however, it appeared to be stable indefinitely.

To test the stability of the hydrazine under reaction conditions, a weighed quantity of the hydrochloride was dissolved in base and the hydrazine was extracted with the dibenzylamine solution to be photolyzed (0.5 M in cyclohexane). The organic layer was dried over sodium sulfate, placed in a photolysis tube, capped, and deaerated. One milliliter was removed with a surgical syringe and analyzed immediately as described above. After photolysis the analytical procedure was repeated and no loss of the hydrazine was apparent.

Photolysis. Product Studies.—Samples were weighed into 10-ml volumetric flasks and diluted to volume with the appropriate solvent. The solution was then transferred to a round quartz tube (15 × 1.5 cm) and deaerated by passing a slow stream of nitrogen through the solution for 10 min. The tube was sealed with a gas-tight rubber septum. The photolyses were carried out in a Rayonet RPR-100 photochemical reactor (The Southern New England Ultraviolet Co.) using 16 253-nm region lamps. The samples were rotated using a Rayonet MGR-100 merry-go-round. Photolysis times varying from 2 to 6 hr showed similar product distributions as did photolyses using 4 rather than 16 lamps.

Photolysis of *N*-Deuteriodibenzylamine [$(PhCH_2)_2ND$].—Equal amounts of the amine (12 g) were placed in two photolysis tubes and deaerated with nitrogen. The tubes were sealed with rubber septa and photolyzed as a neat liquid for 420 min. At the completion of the photolysis the amine mixture was diluted with water and acidified with 8 N sulfuric acid. The aqueous mixture was extracted with three 50-ml portions of ether, and the volume was reduced to one-half the original by distillation. The ether extract was washed with three 10-ml portions of saturated aqueous sodium bisulfite to remove benzaldehyde and with three 20-ml portions of water. The ether layer was then dried over magnesium sulfate and filtered twice through activated charcoal to remove the light yellow coloration which developed during the photolysis. The ether was distilled until the volume was reduced to approximately 0.5 ml. Vpc showed that benzaldehyde was present in amounts corresponding to 1% of the toluene. Preparative vpc on a 4 ft XF 1150 column (100°) was employed to obtain a sample of approximately 15-20 μl of toluene. Pmr analysis in deuteriochloroform showed an intensity ratio of 5.0 to 3.01 for the aromatic to methyl protons, which indicated within experimental error that no deuterium incorporation occurred in the toluene.

Photolysis of Tetrabenzyltetrazene [$(PhCH_2)_2NN{=}NN(CH_2Ph)_2$].—The tetrazene was weighed into a 10-ml volumetric flask and dissolved in spectrograde cyclohexane. The solution was transferred to a Pyrex tube, deaerated with nitrogen, and photolyzed with 310 nm light, to which all products are optically transparent. The nitrogen formed was analyzed by vpc on a 6 ft molecular sieve column using oxygen as an internal marker. Care was taken to prevent air entering either the reaction tube or the syringe used in the analysis. Careful calibrations showed this technique to be quantitative and reproducible.

Thermal Decomposition of Peroxides in the Presence of $(PhCH_2)_2NH$.—Approximately 1.0 mmol of either di-*tert*-butyl peroxide or dicumyl peroxide was weighed directly into a 25-ml round-bottom flask equipped with a side arm for degassing. To this flask was added 15 ml of the neat amine by means of a volumetric pipette. A small reflux condenser was placed on the flask and both the side arm and the top of the condenser were sealed with tight-fitting rubber septa. The contents of the flask was deaerated *via* the side arm by slowly passing nitrogen from a surgical needle through the solution for 35 min.

The decomposition of the peroxide was effected in an oil bath thermostated at 130 ± 2°. The reaction flask was kept in the oil bath for a period of time which varied from 3 to 6 hr. At the completion of the reaction, the contents of the flask was poured into a graduated cylinder. The flask and condenser were washed with two 2-ml portions of acetonitrile, which were combined with the reaction mixture. Acetonitrile was then added to the graduated cylinder to bring the combined volume to 20 ml. Samples were taken from this solution for analysis.

Thermal Decomposition of Dicumyl Peroxide in Dibenzylamine and the Isolation of 4.—Dicumyl peroxide (6.81 g) was weighed into a 250-ml round-bottom flask, and 100 ml of dibenzylamine was added. The flask was fitted with a 3-in. glass adaptor which was capped with a rubber septum. The solution was stirred magnetically and deaerated with a stream of nitrogen for 45 min. The flask was heated with stirring in a silicone oil bath thermostated at 130 ± 2°. On completion, the reaction mixture was distilled under vacuum to remove the liquid fractions which boiled at temperatures corresponding to those of cumyl alcohol and dibenzylamine. The residual liquid, when cooled, yielded a white solid which was recrystallized three times from 95% ethanol. The product was a white amorphous powder: mp 149-150° (lit.[48] mp 151°); pmr[41] δ 1.68 (1.0) (NH) s, 3.4 (2.07) (NCH_2Ph) q, $J \cong$ 1-2 Hz, 3.75 (1.00) (PhCH) s, 7.23 (9.8) (aromatic) m; mass spectrum (70 eV) m/e molecular ion, 392; $PhCHNHCH_2Ph^+$, 196; $PhCH_2NHCHCHPh^+$, 286; $PhCH_2NH^+$, 106; $PhCH_2^+$, 91.

Anal. Calcd for $C_{28}H_{28}N_2$: C, 85.67; H, 7.19; N, 7.14. Found: C, 85.66; H, 7.21; N, 6.92.

Thermal Decomposition of Dicumyl Peroxide in Dibenzylamine in the Presence of O_2.—The procedure for reactions carried out in the presence of oxygen differed little from that where nitrogen was used for degassing. The peroxide and amine were added in a similar manner and the procedure for work-up was the same. In the present case, however, a rubber septum was placed over the side arm and the condenser was connected to a mercury buret of 250-ml capacity. The main body of the buret was filled and emptied twice with oxygen and finally filled with 200 ml of oxygen at atmospheric pressure. After the system was flushed with oxygen, it was placed in the thermostated oil bath and the reaction was allowed to proceed. The oxygen within the flask and buret was maintained at atmospheric pressure and the uptake was monitored continuously until oxygen was no longer absorbed. The contents of the flask were then transferred for analysis as previously described.

The Effect of Acid.—The addition of acid to the photochemical reaction in acetonitrile is shown in Table VII. The only effect observed was a decrease in the free amine present, since the amine was found to undergo its usual photochemical reactions. The inertness of dibenzylammonium trifluoroacetate was at first disturbing, since we felt that it was the aromatic chromophore which was involved in the absorption process leading to reaction. Another study, however, indicated that, while quaternary and tertiary ammonium salts do undergo photodecomposition, secondary and primary salts represented here are inert.[35]

Table VII

Effect of Acid on the Photolysis of Dibenzylamine[a]

			Product, mmol		
Amine[b]	Acid[b,c]	Free amine[b]	$PhCH_3$	$PhCH_2NH$	$PhCH{=}NCH_2Ph$
5.25	1.3	3.95	0.31	0.23	0.31
5.25	2.6	2.65	0.27	0.23	0.29
2.58	0	2.58	0.26	0.20	0.29

[a] Photolysis time, 200 min. [b] Number of millimoles in 10 ml of CH_3CN solution. [c] Trifluoroacetic acid.

Registry No.—**4**, 24431-19-4; dibenzylamine, 103-49-1; tetrabenzylhydrazine, 5416-62-6; tetrabenzyltetrazene, 23456-88-4.

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.

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[48] H. Thies, H. Schonenberger, and K. H. Bauer, *Arch. Pharm.* (*Weinheim*), **291**, 248 (1958); *Chem. Abstr.*, **53**, 3112*d* (1959).