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ALKYLAMINO RADICALS FROM THE PHOTOLYSIS OF BENZYLAMINES

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Abstract—The direct irradiation of a variety of secondary and tertiary N-benzyl-N-alkylamines at 253 nm results in the homolytic scission of only the benzyl-*nitrogen*. The caged pair of benzyl and dialkylamino radicals from tertiary amines are involved in disproportionation. Benzylamine and sec-benzylamines participate in further reactions in which a second nitrogen-centered radical is formed by abstraction from the N—H bond. The combination and disproportionation of various alkylamino radicals are discussed.

INTRODUCTION

THE chemistry of carbon-centered free radicals is reasonably well known, but there is considerably less information on nitrogen-centered free radicals. The photolytic homolysis of amines provides a potentially useful method of generating alkylamino radicals in solution. In this study we examined the photochemical decomposition of benzylamine and its analogs to provide a basis for developing the chemistry of alkylamino radicals.

A series of substituted benzylamines of the form $PhCH_2NHR$ (R = alkyl) were photolyzed directly at 253 nm to investigate how an alkyl group might influence the direction of photodissociation (Eq. (1)).

$$PhCH_2NHR \xrightarrow{h\nu} \begin{cases} PhCH_2\cdot + R\dot{N}H & \text{(1a)} \\ R\cdot + PhCH_2\dot{N}H & \text{(1b)} \end{cases}$$

A second point of interest was to determine the effect of alkyl groups of the fate of the dialkylamino radical undergoing disproportionation to an imine (Eq. (2)). The alkyl substituents which were chosen included

$$PhCH_2\dot{N}CH_2R' + R\cdot \longrightarrow \begin{cases} RH + PhCH{=}NCH_2R' & \text{(2a)} \\ RH + PhCH_2N{=}CHR' & \text{(2b)} \end{cases}$$

methyl as well as primary, secondary and tertiary alkyl groups.

Thirdly, tertiary benzylamines were photolyzed to obtain

$$PhCH_2NR_2 \rightarrow PhCH_2 + R_2\dot{N}, \text{etc.} \qquad (3)$$

direct information of the interaction of alkylamino and alkyl radicals, and to compare the cage disproportionation with that involving secondary amines shown in Eq. (2).

The photolysis of the parent benzylamine itself was also investigated. The products derived from the complex photochemical processes could be accounted for on the basis of the studies of the higher analogs. In the following discussion each of these problems will be treated in order.

RESULTS AND DISCUSSION

The photolysis of N-benzyl-N-t-butylamine was carried out in order to examine the possibility of alkyl cleavage competing with benzyl cleavage in the initial step (Eq. (1)). The t-Bu group could provide the competition suggested by Eq. (1), while at the same time avoiding the problem outlined by Eq. (2), since it has no β-hydrogens capable of undergoing disproportionation.

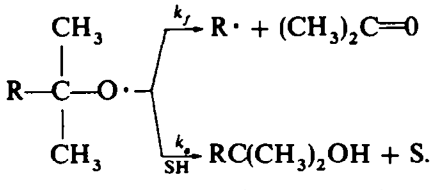
TABLE 1. PHOTOLYSIS OF N-BENZYL-N-t-BUTYLAMINE.[a]

Amine[b]	Solvent	t-$BuNH_2$	$PhCH_3$	$(PhCH_2)_2$	t-BuN=CHPh	t-$BuN(CH_2Ph)_2$
		mmol				
0·31	c-C_6H_{12}	[c]	0·11	0·08	0·22	0·02
0·61	c-C_6H_{12}	[c]	0·18	0·09	0·33	0·04
0·31	CH_3CN	0·91	0·12	0·07	0·15	0·03
0·61	CH_3CN	1·20	0·15	0·09	0·22	0·02

[a] Photolysis time, 360 min. [b] Molar concentration in 10 ml of reaction solution. [c] Yield not determined.

The results shown in Table 1 clearly indicate that only benzyl-nitrogen homolysis occurred. The absence of benzylamine as well as isobutane or isobutylene supports reaction **1a** (R = t-Bu) and limits the possible involvement of t-Bu cleavage.

There are no direct comparative studies available on the relative rates of homolysis of t-butyl-nitrogen and benzyl-nitrogen bonds. However, t-alkoxy radicals have been examined in detail,[1] and the relative rates of β-scission and hydrogen abstraction are given by k_f/k_a in Eq. (4). The ratios of k_f/k_a can be used to obtain comparative rates of fragmentation since the value k_a is not expected to vary drastically with the structure of R.

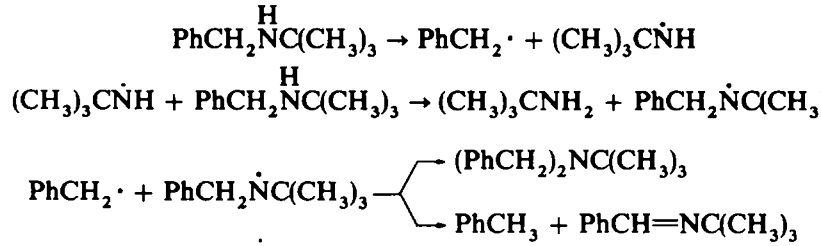


$$R\text{—}C(CH_3)_2\text{—}O\cdot \xrightarrow{k_f} R\cdot + (CH_3)_2C{=}O \qquad (4a)$$

$$R\text{—}C(CH_3)_2\text{—}O\cdot \xrightarrow[SH]{k_a} RC(CH_3)_2OH + S\cdot \qquad (4b)$$

Since this rate ratio is approximately the same for R = t-Bu and benzyl,[2] we surmise that a reaction leading to the competitive expulsion of these radicals would be rather unselective. However, results in Table 1 show that no products arising from the cleavage of the t-butyl-nitrogen bond (benzylamine, C_4-hydrocarbons) were present. In the absence of direct physical studies, we conclude that the photochemical reactions proceed by the absorption of radiant energy into the aromatic chomophore. Electronic transitions involving the non-bonded electrons on nitrogen, as in simpler alkylamines,[3–6] do not appear to be important. Support for this formulation is also available from the photolysis of benzylammonium salts, in which the non-bonded electrons no nitrogen are no longer available, but nonetheless these salts undergo facile photodecomposition at these wavelengths.[7]

The products and the stoichiometry of the photodecomposition of N-t-butyl-N-benzylamine is consistent with the following scheme:



$$PhCH_2\overset{H}{N}C(CH_3)_3 \rightarrow PhCH_2\cdot + (CH_3)_3C\dot{N}H \qquad (5)$$

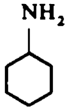
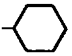
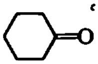
$$(CH_3)_3C\dot{N}H + PhCH_2\overset{H}{N}C(CH_3)_3 \rightarrow (CH_3)_3CNH_2 + PhCH_2\dot{N}C(CH_3)_3 \qquad (6)$$

$$PhCH_2\cdot + PhCH_2\dot{N}C(CH_3)_3 \rightarrow (PhCH_2)_2NC(CH_3)_3 \qquad (7a)$$

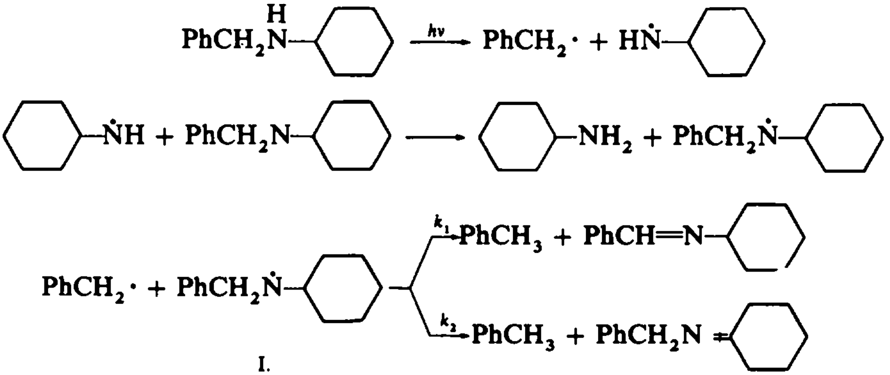
$$PhCH_2\cdot + PhCH_2\dot{N}C(CH_3)_3 \rightarrow PhCH_3 + PhCH{=}NC(CH_3)_3 \qquad (7b)$$

The photolysis of N-benzyl-N-cyclohexylamine was undertaken to study the disprotortionation step (Eq. (2)). The products resulting from disproportionation afford benzaldehyde and cyclohexanone after hydrolysis, and they are both relatively easy to analyze quantitatively. The photolysis of benzylcyclohexylamine was carried out in n-hexane and acetonitrile solutions and the results shown in Table 2. Cyclohexane was absent, as expected from the previous study. Competition from the disproportionation step was indicated by the presence of both benzylidenecyclohexylamine and cyclohexylidenebenzylamine. The latter also provide evidence that radical I formed in the primary dark reaction[9] has the general structure $R\text{—}\dot{N}\text{—}R'$. A rough estimate of $k_1/k_2 = 2$ is obtained, if it is assumed that the imines arise by Eq. (10), and that which might result from the disproportionation

TABLE 2. PHOTOLYSIS OF BENZYLCYCLOHEXYLAMINE.[a]

Amine[b]	Solvent		$PhCH_3$	$(PhCH_2)_2$	$(PhCH_2)_2N$- 	PhCHO[c]	 [c]
		mmol					
0·27	n-C_6H_{12}	0·67	0·20	0·10	0·09	—	—
0·54	n-C_6H_{12}	0·89	0·28	0·12	0·13	—	—
0·25	CH_3CN	0·63	0·20	0·10	0·19	0·19	0·05
0·59	CH_3CN	0·85	0·25	0·12	—	0·24	0·06

[a] Photolysis time, 420 min. [b] Molar concentration in 10 ml of reaction solution. [c] Only after acid hydrolysis.



(8)

(9)

(10a)

(10b)

I.

of two benzylcyclohexylamino radicals I is neglected. The value is based on the yields of carbonyl compounds after correcting for the number of available hydrogens. No dimers which could result from the N-centered radical I were found. There was also no indication for the removal of the benzylic hydrogen in Eq. (9) (or in Eq. (6)), since such a process would ultimately lead to 1,2-diphenylethylamines.[8]

The material balance for the products resulting from the radicals produced in the initial homolysis was reasonably good. Thus, the combined yield of all the products derived from benzyl radicals (Σ $PhCH_2\cdot$) was equal to 88% of the yield of cyclohexylamine for photolyses carried out in acetonitrile and 75% in cyclohexane.

Photolysis of tertiary benzylamines

The photolysis of tertiary benzylamines provides a method of generating a benzyl radical and a secondary amino radical directly (Eq. (11)).

$$PhCH_2NR(R') \xrightarrow{h\nu} Ph\dot{C}H_2 + R\dot{N}R' \tag{11}$$

This radical pair must be more intimately associated than that derived from the photolysis of secondary amines presented in Eqs. (7) and (10), since radical pairs are formed from the latter only after chain transfer (compare Eqs (6) and (9)). Such a distinction can be shown by a comparative study of the photolysis of N,N,N-*tribenzylamine* and N,N-*dibenzylamine.*

N,N,N-*Tribenzylamine*

The results of the photolysis of N,N,N-tribenzylamine are listed in Table 3. The mass balance among the products in Table 3 was good for all runs, even after extended periods of photolysis. Filtering of the light by N-benzylbenzaldimine is apparently responsible for the lack of secondary photolysis, despite the prolonged periods of irradiation.

The formation of products and concomitant decrease of the starting material is shown in Fig 1, as a function of time, for the photolysis of 0·175 M solution of tribenzylamine in cyclohexane. The reaction was followed to approximately 65% completion (based on starting amine). The product distribution indicates that little or no secondary photolysis occurred. The mass balance for the photolysis given in Table 4 shows that greater than 90% of all of the products resulting from both the benzyl radicals as well as the alkylamino radicals can be accounted for.

TABLE 3. PHOTOLYSIS OF N,N,N-TRIBENZYLAMINE.

Amine[a]		Solvent	$PhCH_3$	$(PhCH_2)_2$	$PhCH{=}NCH_2Ph$	PhCHO[d]	$(PhCH_2)_2NH$
(start)[e]	(recover)		mmol				
1·76[c]	0·63	c-C_6H_{12}	0·79	—	0·75	0·80	0·26
1·75[c]	0·78	c-C_6H_{12}	0·76	0·08	0·71	0·79	0·22
4·65[b]	—	c-C_6H_{12}	0·65	0·09	0·65	—	0·22
1·76[c]	0·71	CH_3CN	0·66	—	0·80	0·74	0·21
1·75[c]	0·86	CH_3CN	0·66	0·09	0·70	0·76	0·21

[a] mmol. [b] Photolysis time, 200 min. [c] Photolysis time, 400 min. [d] Only after acid hydrolysis. [e] In 10 ml solvent.

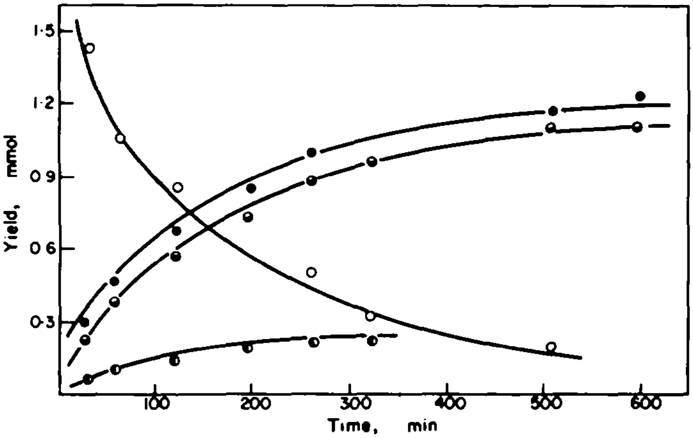


FIG 1. The rate of photolysis of tribenzylamine. ⦶, dibenzylamine; ⊖, toluene; ●, N-benzylbenzaldimine; ○, tribenzylamine.

If radicals formed in the homolysis of tribenzylamine were randomly distributed in solution, the probability that a benzyl radical will encounter another benzyl radical would be one-half that of an amino radical. The low yields of bibenzyl, however, suggest that the radicals are not distributed statistically (provided there is no selectivity in the combination). A cage mechanism (Eq. (13)) offers the most reasonable explanation for the high yields of toluene and N-benzylbenzaldimine generated by the cross disproportionation of benzyl and dibenzylamino radicals.

TABLE 4. MASS BALANCE FOR THE PHOTOLYSIS OF TRIBENZYLAMINE.

Amine lost mmol	Σ PhCH$_2$[a] mmol (%)[c]	ΣN Products[b] mmol (%)[c]
1·13	—	1·01 (90)
0·97	0·92 (95)	0·93 (96)
1·05	—	0·87 (83)
0·89	0·84 (95)	0·91 (102)

[a] Toluene plus 2 bibenzyl. [b] Dibenzylamine plus N-benzylbenzaldimine.
[c] Based on amine lost.

$$(PhCH_2)_3N \underset{k_r}{\overset{h\nu}{\rightleftharpoons}} [Ph\dot{C}H_2, \dot{N}(CH_2Ph)_2] \tag{12}$$

$$[PhCH_2\cdot, \dot{N}(CH_2Ph)_2] \begin{cases} \xrightarrow{k_r} PhCH_3 + PhCH_2N{=}CHPh & (13a) \\ \xrightarrow{k_d} PhCH_2\cdot + (PhCH_2)_2\dot{N} & (13b) \end{cases}$$

$$2\,PhCH_2\cdot \rightarrow PhCH_2CH_2Ph \tag{14}$$

$$2(PhCH_2)_2\dot{N} \rightarrow (PhCH_2)_2NH + PhCH{=}NCH_2Ph \tag{15}$$

N,N-*Dibenzylamine*

The results in Table 5 indicate that dibenzylamino radicals must also be important intermediates in the photolysis of N,N-dibenzylamine. N,N-dibenzylamino radicals cannot be formed in the primary process, and we propose the following scheme to account for these observations.[*]

$$(PhCH_2)_2NH \overset{h\nu}{=} Ph\dot{C}H_2 + PhCH_2\dot{N}H \tag{16}$$

$$PhCH_2\dot{N}H + (PhCH_2)_2NH \rightarrow PhCH_2NH_2 + (PhCH_2)_2\dot{N} \tag{17}$$

$$PhCH_2\cdot + (PhCH_2)_2N\cdot \longrightarrow \begin{cases} (PhCH_2)_3N & \text{(18a)} \\ PhCH_3 + PhCH_2N{=}CHPh & \text{(18b)} \end{cases}$$

Interestingly, we could find no evidence in the photolysis of dibenzylamine for the cage disproportionation of benzyl and benzylamino radicals. The latter is consistent with the photolysis of N-benzyl-N-t-butylamine given in Eqs. (5) to (7), in which disproportionation of benzyl and t-butylamino radicals is impossible (compare the results in Tables 1 and 5). Furthermore, the chain transfer reaction between benzylamino radical and dibenzylamine in Eq. (17) does not afford the carbon-centered radical by abstraction of a benzylic hydrogen. These benzylic radicals can be generated independently by autoxidation of N,N-dibenzylamine or reaction with alkoxy radicals, and

TABLE 5. PHOTOLYSIS OF N,N-DIBENZYLAMINE.[a]

Amine (M)	Solvent	$PhCH_3$	$PhCH_2NH_2$	$PhCH{=}NCH_2Ph$	$(PhCH_2)_3N$	$(PhCH_2)_2$
		mmol				
0·15	$c\text{-}C_6H_{12}$	0·06	0·06	0·09	0·02	0·02
0·20	$c\text{-}C_6H_{12}$	0·10	0·07	0·10	0·02	0·025
0·25	CH_3CN	0·09	0·07	0·09	0·04	0·027
0·50	CH_3CN	0·11	0·11	0·11	0·06	0·030

[a] Photolysis time, 60 min.

$$(CH_3)_3C\dot{O} + (PhCH_2)_2NH \rightarrow (CH_3)_3COH + PhCH_2NH\dot{C}HPh \tag{19}$$

further reactions consist of disproportionation as well as combination (Eq. (20b))[8]. The latter, however, is absent in the photochemical process.

$$2\,PhCH_2NH\dot{C}HPh \longrightarrow \begin{cases} PhCH_2N{=}CHPh + (PhCH_2)_2NH & \text{(20a)} \\ \begin{array}{l} PhCH_2NHCHPh \\ PhCH_2NHCHPh \end{array} & \text{(20b)} \end{cases}$$

Thus, the mechanistic schemes proposed above for the photolysis of N,N,N-tribenzylamine and N,N-dibenzylamine have certain features in common. The major

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[*] A more extensive experimental support for this scheme is given in ref. 8.

distinction between them, however, lies in the idea that the two radicals are produced directly in the former. As a consequence, the initial distance of separation of the radical pair is less than that for the same pair of radicals derived from the photolysis of dibenzylamine. This difference is reflected in a higher yield of toluene relative to bibenzyl, the relative ratios of which reflect the "cage" and "non-cage" processes (cf. Tables 3 and 5). From the photolysis of tribenzylamine, a value of about 10 was found for the relative yields of toluene and bibenzyl. A value this large in the photolysis of dibenzylamine was attained only in highly viscous media.[8]

The recombination of the benzyl and dibenzylamino fragments (k_r in Eq. (12)) cannot be obtained from our data, and stereochemical studies would be highly informative. However, values of k_p/k_r can be estimated for this radical pair from the relative amounts of tribenzylamine and toluene obtained in the photolysis of dibenzylamine. From these data a value of k_p/k_r about 2–5 was obtained.

It should be emphasized that the values for the ratios of rate constants obtained above are only approximations, since complications due to product formation outside the cage make values for k_p/k_d and k_p/k_r difficult to obtain.[*] The trends, however, support the hypothesis that large percentages of these reactions occur before the distribution of radicals becomes statistical.

TABLE 6. PHOTOLYSIS OF TERTIARY DIBENZYLAMINES.

$(PhCH_2)_2NR$ (start)	(recover)	Solvent	$PhCH_3$	$(PhCH_2)_2$	$PhCH_2\overset{H}{N}R$[a]	$PhCH{=}NR$[a]	$PhCHO$[e]
			mmol				
R = $C(CH_3)_3$[b]							
1·0	0·50	$c\text{-}C_6H_{12}$	0·42	0·08	0·09	0·61	—
2·0	1·34	$c\text{-}C_6H_{12}$	0·62	0·12	0·12	0·82	—
R = $c\text{-}C_6H_{11}$[c]							
0·9	—	$n\text{-}C_6H_{14}$	0·37	0·11	0·26	—	—
1·9	—	$n\text{-}C_6H_{14}$	0·59	0·16	0·40	—	—
0·9	—	CH_3CN	0·30	0·07	0·21	—	0·35[f]
R = $(CH_2)_5CH_3$[d]							
0·95	—	CH_3CN	0·36	0·09	0·02	—	0·27[g]
1·9	—	CH_3CN	0·59	0·12	0·04	—	0·42

[a] R is corresponding alkyl group. [b] Photolysis time, 360 min. [c] Photolysis time, 420 min. [d] Photolysis time, 450 min. [e] Only after acid hydrolysis. [f] In addition to PhCHO, approximately 0·03–0·04 mmol cyclohexanone was formed. [g] Trace amounts of hexanal were also formed. [h] In 10 ml solvent.

N,N-*Dibenzyl*-N-*alkylamines*. The same alkyl substituents employed in the photolysis of secondary benzylamines were also used in the study of tertiary benzylamines listed in Table 6. Acceptable mass balance and product distributions were obtained for all reactions carried out to greater than 50% completion. In each case the photolysis of tertiary amines afforded reactions whose stoichiometries were less ambiguous than those examined with the corresponding secondary amines. The yields of the products derived from the benzyl radical and the alkylamino radical are within 15% of one another. Furthermore, there was no evidence (Table 6) that alkyl cleavage

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[*] Unfortunately, cage and noncage process cannot be differentiated with scavengers in this system, since most of the reactive ones are not optically transparent at 253 nm.

occurred to any significant extent in the systems studied, as expected from the results of photolysis of the secondary amines.

All three amines in Table 6 afforded on photolysis lower ratios of toluene relative to bibenzyl than did tribenzylamine. These values are higher, however, than those obtained from the correspondingly substituted secondary amines. Some disproportionation to the alkyl side was found to occur in both the cyclohexyl and n-hexyl benzylamines. The data for cyclohexanone and hexanal formation were not accurate enough to obtain a reliable number for the selectivity, but an estimate for k_1/k_2 of about 5 for the competition in Eq. (10) can be obtained from the cyclohexanone yield. The same ratio was 2 when calculated from the results for benzylcyclohexylamine. For the secondary amine, however, contributions from the self reaction of two benzylcyclohexylamino radicals were neglected. Encounter between this pair is expected to be greater for the secondary than for the tertiary amine, and it should not necessarily show the same selectivity in disproportionation.

Photolysis of benzylamine...

The photolysis of the structurally simplest amine of the series, benzylamine, yielded the most complex product distribution. The results, however, can be interpreted within the same general framework described for the secondary and tertiary benzylamines. Thus, the photolysis of benzylamine resulted in the production of large quantities of N,N-dibenzylamine and N-benzylbenzaldimine along with ammonia as the major nitrogenous products. Small amounts of tribenzylamine were also formed. The yield of ammonia was greater than that of the other nitrogenous products, except when the amine was photolyzed neat. In the latter case the correlation between the yields of ammonia and the products derived from the benzyl radical was better, since 85–95% of the benzyl groups could accounted for on the basis of the ammonia formed. The results are shown in Table 7.

TABLE 7. PHOTOLYSIS OF BENZYLAMINE.

Amine	Solvent	NH_3	$PhCH_3$	$(PhCH_2)_2$	$(PhCH_2)_2NH$	$PhCH{=}NCH_2Ph$	$PhCHO$[g]
		mmol					
neat[a]	none	1·3	0·24	0·05	0·70	0·36	0·32
4·82(4.16)[a,e]	$c\text{-}C_6H_{12}$	—	0·11	0·02	0·13	0·12	—
5·08(4·7)[a,e]	$c\text{-}C_6H_{12}$	—	—	0·02	0·125	0·125	—
0·47[b,d,f]	$c\text{-}C_6H_{12}$	0·21	0·05	—	0·06	0·09	—
0·84[b,d]	$c\text{-}C_6H_{12}$	0·50	0·09	—	0·15	0·153	—
1·83[b,d]	$c\text{-}C_6H_{12}$	0·95	0·15	—	0·30	0·24	—
4·73(3·2)[c,e]	CH_3CN	1·2	0·13	0·04	0·22	0·24	0·29

[a] Photolysis time, 420 min. [b] Photolysis time, 230 min. [c] Photolysis time, 650 min. [d] Molar concentrations. [e] mmol in 10 ml solution. Figure in parentheses is amine recovered. [f] 0·01 mmol $(PhCH_2)_3N$. [g] After hydrolysis.

Since the yield of benzaldehyde after hydrolysis was equivalent to that of the N-benzylbenzaldimine, only minor amounts of other benzaldehyde precursors (e.g. $PhCH{=}NH$) could have been present in the photolysate. The following reactions can be considered:

$$\mathrm{PhCH_2NH_2} \xrightarrow{h\nu} \mathrm{PhCH_2\cdot} + \dot{\mathrm{N}}\mathrm{H_2} \tag{21}$$

$$\mathrm{PhCH_2NH_2} + \dot{\mathrm{N}}\mathrm{H_2} \rightarrow \mathrm{PhCH_2\dot{N}H} + \mathrm{NH_3} \tag{22}$$

$$\mathrm{PhCH_2\cdot} + \mathrm{PhCH_2\dot{N}H} \rightarrow (\mathrm{PhCH_2})_2\mathrm{NH} \tag{23a}$$

$$\mathrm{PhCH_2\cdot} + \mathrm{PhCH_2\dot{N}H} \rightarrow \mathrm{PhCH_3} + \mathrm{PhCH{=}NH} \tag{23b}$$

$$\mathrm{PhCH{=}NH} + \mathrm{PhCH_2NH_2} \rightarrow \mathrm{PhCH{=}NCH_2Ph} + \mathrm{NH_3} \tag{24}$$

$$(\mathrm{PhCH_2})_2\mathrm{NH} + \dot{\mathrm{X}} \rightarrow (\mathrm{PhCH_2})_2\dot{\mathrm{N}} + \mathrm{XH},\ \text{etc.} \tag{25}$$

$$[\mathrm{X} = \dot{\mathrm{N}}\mathrm{H_2} \text{ or } \mathrm{PhCH_2\dot{N}H}]$$

The nitrogen dimer, sym-dibenzylhydrazine, was not observed although small amounts equivalent to bibenzyl would have been difficult to detect due to its extreme sensitivity to air.[8] Nonetheless, support for N—H abstraction in Eq. (22) derives largely from the products formed (i.e. dibenzylamine, N-benzylbenzaldimine, tribenzylamine) and the absence of dimers involving the carbon-centered radical, $\mathrm{Ph\dot{C}HNH_2}$ (experimental). The observation of small but significant amounts of N,N,N-tribenzylamine also indicates that attack at the N—H bond follows the general trend in radical stability, i.e. $\mathrm{R_2\dot{N}} > \mathrm{R\dot{N}H} > \mathrm{H_2\dot{N}}\cdot$[9]

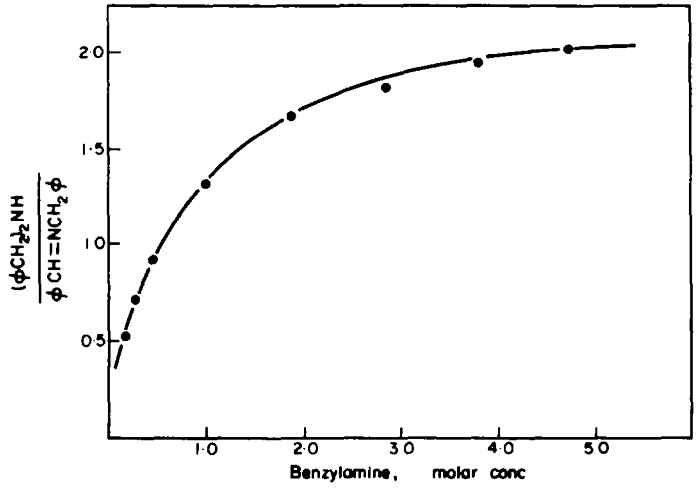


FIG 2. The influence of the initial benzylamine concentration on the product ratio.

N-benzylbenzaldimine is a major product and may be formed either *via* transamination of benzaldimine (Eq. (24))[10] or disproportionation of the dibenzylamino radical generated in Eq. (25). The latter is supported by concentration studies (Table 8) carried out in cyclohexane solutions. Thus, Fig 2 shows that the amounts of dibenzylamine increase relative to N-benzylabenzaldimine as the initial concentration of benzylamine is increased. At low benzylamine concentrations, the initially formed dibenzylamine competes more effectively with benzylamine for the amino radicals (cf. Eqs (22) and (25)). Consequently, at the low amine concentrations a greater fraction of the reaction proceeds *via* the dibenzylamino radical, which affords imine by subsequent

TABLE 8. EFFECT OF BENZYLAMINE CONCENTRATION ON PRODUCT DISTRIBUTION.[b]

Amine[a]	$(PhCH_2)_2NH$	$PhCH{=}NCH_2Ph$	$(PhCH_2)_2NH$[c] / $PhCH{=}NCH_2Ph$
	mmol		
0·16	0·026	0·051	0·51
0·25	0·047	0·065	0·72
0·49	0·096	0·10	0·91
0·99	0·185	0·142	1·30
1·89	0·317	0·190	1·67
2·84	0·42	0·234	1·80
3·76	0·513	0·263	1·95
4·71	0·665	0·33	2·0

[a] Molar concentration in CH_3CN (10 ml). [b] Photolysis time 442 min. [c] Neat benzylamine gave a value of approximately 2 (Table 7).

disproportionation. At higher concentrations of benzylamine, the dibenzylamine is less able to compete as a hydrogen donor. Alternative explanations involving changes in the viscosity of the medium are less attractive.

SUMMARY AND CONCLUSIONS.

The direct photolyses of a series of primary, secondary and tertiary N-benzyl-N-alkylamines proceed by homolysis of only the benzyl-nitrogen bond. The principal dark reaction subsequent to homolysis of tertiary amines is the cage disproportionation of the benzyl and dialkylamino radicals. Secondary amines and benzylamine also undergo only benzyl-nitrogen photolysis. However, the availability of N—H bonds in these compounds allow the alkylamino radical to undergo chain transfer to generate a series of second generation nitrogen-centered radicals. Abstraction of benzylic hydrogens or cage disproportionation do not appear to be important reactions with amino or alkylamino radicals. The differences can also be attributed to the changes in the reactivity of the amino radicals with alkyl substitution, i.e.

$$\dot{N}H_2 > R\dot{N}H > R_2\dot{N}$$

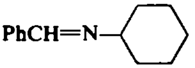
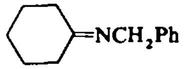
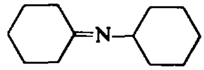
The latter also follows from their thermodynamic stabilities listed below.[11]

Amino Radical	Heat of formation (kcal mole^{-1})
$\dot{N}H_2$	47·2
$CH_3\dot{N}H$	45·2
$(CH_3)_2\dot{N}$	38·2

EXPERIMENTAL

Aliphatic amines. Aliphatic amines used in synthesis were routinely stored over KOH for 24 hr and distilled. The solvents used in these experiments were treated in a manner similar to that described previously.[8] Benzylamine was dissolved in dioxane and gaseous HCl bubbled through the soln for several min. The hydrochloride was filtered, washed with dioxane and ether and recrystallized three times from EtOH yielding long flat needles. The amine was liberated by dissolving the salt in water and heating the soln with excess $NaHCO_3$ at 70° for 1 hr. The amine was quantitatively removed from the water by continuous extraction with ether for 12 hr. The ether was removed by rotary evaporation and the amine distilled under vacuum. bp 65° (1.0 mm Hg). All imines (aldimines and ketimines) were prepared by mixing equimolar amounts of the corresponding amine and aldehyde (ketone) in benzene.[12] The resulting soln was heated to reflux and the water removed by azeotropic distillation with a Dean-Stark trap. After removal of the theoretical amount of water the soln was cooled and the benzene removed by rotary evaporation. The imines were then distilled under reduced pressure (Table 9). All secondary amines were prepared by the catalytic reduction of the corresponding benzaldimine.

TABLE 9. IMINES.

imine	bp (°C)	(mm Hg)	Spectral data Table 14
$PhCH{=}NCH_2Ph$	160–165	(5)	1
$PhCH{=}N{-}C(CH_3)_3$	104–106	(20)	2
	88–92	(0·25)	5
	95–105	(0·25–0·5)	6
	73–75	(0·25)	7
$PhCH{=}NCH_2(CH_2)_4CH_3$	82–83	(0·25)	10
$CH_3(CH_2)_4CH{=}NCH_2Ph$	138–139	(0·20)	11
$PhCH_2CH_2N{=}CHPh$	m.p. 37–39°C		14

Ten to twenty grams of the imine was mixed with approximately 100 ml of 95% EtOH and 0·5 g of 5% Pd/C in a pressure flask. The flask was placed on a parr reduction apparatus and flushed several times with H_2. Reduction was allowed to proceed until the H_2 uptake ceased (4 to 6 hr). The contents were filtered through a medium sintered glass funnel with celite filter-aid and the ethanol removed by rotary evaporation.

The amines were purified by distillation under vacuum (Table 12). PMR analysis indicated the reductions were quantitative with little, if any, hydrogenolysis occurring. *Tertiary amines.* Equimolar amounts of benzyl bromide and the necessary secondary amine were heated in DMSO for 24 hr at 70°. Solid Na_2CO_3 (excess) was added to the cooled soln which was then stirred at 70° for 1 hr. The cooled mixture was diluted with a large volume of water and extracted with three portions of ether. The combined ether extracts was washed several times with water to remove residual DMSO and the ether removed by rotary evaporation. The amines were recrystallized from acetonitrile (Table 11).

TABLE 10. SECONDARY AMINES.

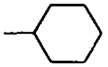
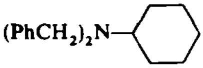
	$\overset{H}{RNR'}$			
R	R'	bp (°C)	(mm Hg)	Spectral data Table 14
$PhCH_2$-	$-C(CH_3)_3$	90–91	(13)	3
$PhCH_2$-		103–105	(0·5)	8
$PhCH_2$-	$-CH_2(CH_2)_4CH_3$	75–77	(0·2)	12
$PhCH_2$	$-CH_2CH_2Ph$	180–181	(8·5)	15

TABLE 11. TERTIARY AMINES.

Amine	m.p. (°C)	Spectral data Table 14
$(PhCH_2)_2N—C(CH_3)_3$	70·5–71	4
	61–62	9
$(PhCH_2)_2NCH_2(CH_2)_4CH_3$	b.p. 135°C (0·1 mm Hg)	13

Photolysis. The sample preparation, the photochemical methods and the quantum yield studies were described previously.[8]

N-Benzyl-N-n-hexylamine was studied as an example of a secondary amine containing a primary alkyl group. The major observation from the photolysis of this compound was the poor mass balance obtained in comparison to that obtained from the cyclohexyl or t-butyl analogs (Table 12).

TABLE 12. PHOTOLYSIS OF N-BENZYL-N-n-HEXYLAMINE.

Amine[a]	Solvent	$nC_6H_{13}NH_2$	$PhCH_3$	$(PhCH_2)_2$	$(PhCH_2)_2N(CH_2)_5CH_3$	PhCHO[e]
		mmol				
0·13[b]	$c\text{-}C_6H_{12}$	0·22	0·17	—	—	0·04
0·27[b]	$c\text{-}C_6H_{12}$	0·30	0·18	—	—	0·06
0·13[c]	CH_3CN	0·32	0·24	0·08	0·02	0·03
0·27[c]	CH_3CN	0·46	0·30	0·10	0·06	0·08
neat[d]	—	0·73	0·31	—	0·16	0·18

[a] Molar concentration in 10 ml reaction solution. [b] Photolysis time, 200 min.
[c] Photolysis time, 450 min. [d] Photolysis time, 420 min. [e] After acid hydrolysis.

Although the relationship between the yields of benzyl products ($\Sigma PhCH_2\cdot$) and the yield of the primary amine remained good, the correspondence between the yields of toluene and aldehyde (after hydrolysis) was unusually poor. Only when the amine was photolyzed neat did the aldehyde yield become appreciable, and then it accounted for only 60% of the toluene formed. Only trace amounts of hexanal were found.

The stability of the imine $[PhCH{=}N{-}(CH_2)_5CH_3]$ under reaction conditions was tested by photolyzing small quantities of it in solutions containing either dibenzylamine or benzyl-n-hexylamine. In all cases benzaldehyde could be found after hydrolysis in amounts corresponding to quantitative recovery. However, it is possible that some of the difficulty may have arisen from further attack on the isomeric n-*hexylidene* imine $[CH_3(CH_2)_4CH{=}NCH_2Ph]$. Thus, the ready abstraction of the vinylic hydrogen of imines has been recently reported.[13]

TABLE 13. PHOTOLYSIS OF N-BENZYL-N-METHYLAMINE.[a]

Amine[b]	Solvent	$PhCH_3$	$(PhCH_2)_2$	$(PhCH_2)_2NCH_3$	PnCHO[c]
		mmol			
0·50	$c\text{-}C_6H_{12}$	0·12	0·02	0·05	—
1·0	$c\text{-}C_6H_{12}$	0·14	0·02	0·08	—
1·0	CH_3CN	0·08	0·03	—	0·10

[a] Photolysis time, 60 min. [b] Molar concentration in 10 ml reaction solution. [c] Only after acid hydrolysis.

The unusually poor mass balance obtained from the photolysis of benzyl-n-hexylamine prompted us to examine another secondary benzylamine containing a primary alkyl moiety. The photolysis of N-benzyl-N-methylamine afforded substantial yields of benzaldehyde (Table 13), which are more in keeping with the results obtained with other alkyl substituted benzylamines.

The photolysis of N-benzyl-N-methylamine shown in Table 13 proceeds exclusively by homolysis of the benzyl–nitrogen bond. The disproportionation of the N-benzyl-N-methylamino radical favored loss of the benzylic hydrogen.

Product analysis. All analytical methods used here are the same as those described for the photolysis of dibenzylamine.[8] Ammonia formed during the photolysis of benzylamine was analyzed by titration after first removing it from the other basic materials. The ammonia was removed from the capped photolysis tube by entraining it with a stream of N_2 through a scrubbing tube of ice-cold n-hexane and into a standard HCl soln. The excess acid was back-titrated in the presence of methyl red indicator. A series of standard runs, in which the concentrations of both ammonia and benzylamine were varied, showed the method to be quantitative within the limits of the titration.

α-Benzildioxime. PhC(NOH)C(NOH)Ph. NaOH (80 g) was dissolved in 500 ml water and 40 g hydroxylamine hydrochloride added (with cooling) followed by 50 g powdered benzil and 25 ml EtOH. The mixture was stirred mechanically at room temp for 3 days (the time is important). The oxime was precipitated by the addition of solid CO_2, filtered and washed with boiling EtOH, m.p. 228–230° (lit.[14] m.p. 230°).

1, *2-Diphenylethylenediamine.* PhCH(NH_2)CH(NH_2)Ph. In a round bottom flask, 12·5 g α-benzildioxime was covered with 200 ml abs EtOH. A reflux condenser was placed on the flask and 35 g Na added slowly

TABLE 14. SPECTRAL DATA.

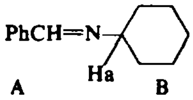
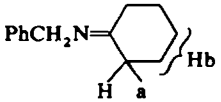
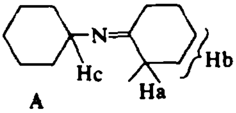
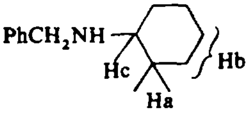
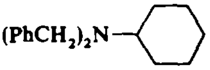
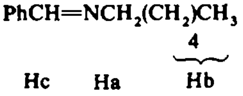
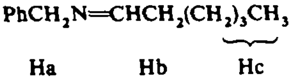
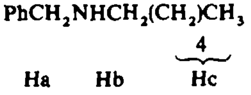
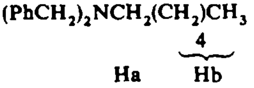
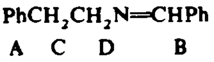
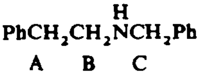
Compound	PMR				IR	
	a	*b*	*c*	*d*	*e*	*f*
1. PhCH=NCH$_2$Ph A B	3·91	(1·95)	(—CH_2—)	s	6·1	(m)
	6·52	(7·93)	(B and *m*, *p*, *A*)m		8·3	(2)
	7·08	(2·02)	(*o*, A)m		13·3	(s)
	7·35	(1·0)	(—CH=)s		14·4	(s)
2. PhCH=NC(CH_3)$_3$	0·97	(8·93)	(c(C$\underline{H}_3$)$_3$)s			
	7·0	(3·1)	(*m*,*p*, aromatic)m			
	7·45	(1·95)	(*o*, aromatic)m			
	7·88	(1·0)	(—CH=)s			
3. PhCH$_2$NHC(CH_3)$_3$	1·0	(1·0)	(NH)s			
	1·09	(8·7)	(C(CH_3)$_3$)s			
	3·68	(2·02)	(—CH_2—)s			
	7·31	(5·0)	(aromatic)m			
4. PhCH$_2$)$_2$NC(CH_3)$_3$	1·12	(9·07)	(C(CH_3)$_3$)s			
	3·7	(4·0)	(—CH_2—)s			
	7·16	(9·96)	(aromatic)m			
5. 	1·56	(10·9)	(B)m(broad)		6·1	(s)
	3·1	(0·94)	(Ha)s(broad)		6·9	(s)
	7·27	(3·18)	(*m*,*p*, A)m		13·2	(s)
	7·70	(2·06)	(*o*, A)m		14·4	(s)
	8·18	(1·0)	(—CH=)s			
6. 	1·55	(6·4)	(Hb)m(broad)			
	2·2	(4·5)	(Ha)m(broad)			
	4·4	(2·0)	(—CH_2—)s			
	7·25	(5·2)	(aromatic)s			

TABLE 14. SPECTRAL DATA—*continued*.

Compound	PMR	IR
	a *b* *c* *d*	*e* *f*
7. 	1·5 (—)(A,Hb)m(broad) 2·21 (4.3) (Ha)s(broad) 3·23 (1·0) (Hc)s(broad)	
8. 	0·88 (1·1) (—NH—)s 0·9 to 2·1 (10·0) (Ha, Hb)m(broad) 2·35 (0·93) (Hc)s(broad) 3·70 (2·0) (—CH_2—)s 7·16 (5·0) (aromatic)m	
9. 	0·9 to 2·3 (11.1) (A)m(broad) 3·67 (4·0) (—CH_2—)s 7·28 (10·7) (aromatic)m(broad)	
10.  $\underset{\mathrm{Hc}}{\mathrm{PhCH}}{=}\underset{\mathrm{Ha}}{\mathrm{NCH_2}}\underset{\mathrm{Hb}}{\underbrace{\underset{4}{\mathrm{(CH_2)CH_3}}}}$	0·7 to 1·8 (—) (Hb)m(broad) 3·5 (1·90) (Ha)t 7·25 (3·0) (*m*,*p*,aromatic)m 7·62 (1·94) (*o*,aromatic)m 8·12 (1·0) (Hc)s	
11.  $\underset{\mathrm{Ha}}{\mathrm{PhCH_2N}}{=}\underset{\mathrm{Hb}}{\mathrm{CHCH_2}}\underset{\mathrm{Hc}}{\underbrace{\mathrm{(CH_2)_3CH_3}}}$	0·90 and 1·4 (—) (Hc)m(broad) 2·3 (—) /Hb)m(broad) 4·62 (2·0) (—CH_2—)s 7·22 (5·4) (aromatic)s 7·80 (1·0) (Ha)s	
12.  $\underset{\mathrm{Ha}}{\mathrm{PhCH_2}}\underset{\mathrm{Hb}}{\mathrm{NHCH_2}}\underset{\mathrm{Hc}}{\underbrace{\underset{4}{\mathrm{(CH_2)CH_3}}}}$	1·0 and 1·4 (12 with NH)(Hc)m(broad) 1·2 (12 with Hc) (NH)s 2·65 (2·0) (Hb)t(broad) 3·80 (2·0) ($\phi C\underline{H}_2$—)s 7·28 (5·0) (aromatic)s	
13.  $\mathrm{(PhCH_2)_2}\underset{\mathrm{Ha}}{\mathrm{NCH_2}}\underset{\mathrm{Hb}}{\underbrace{\underset{4}{\mathrm{(CH_2)CH_3}}}}$	0·85 and 1·25 (11·1) (Hb)m(broad) 2·40 (1·93) (Ha)t(broad) 3·53 (4·0) ($\phi C\underline{H}_2$—)s 7·25 (10·0) (aromatic)m	
14.  $\underset{\mathrm{A}}{\mathrm{Ph}}\underset{\mathrm{C}}{\mathrm{CH_2}}\underset{\mathrm{D}}{\mathrm{CH_2}}\mathrm{N{=}CH}\underset{\mathrm{B}}{\mathrm{Ph}}$	2·97 (2·03) (C)t 3·81 (2·0) (D)t 7·24 (7·86) (A; *m*, *p*, B)m 7·65 (2·0) (*o*, B)m 8·05 (1·06) (=$C\underline{H}\phi$)s	
15.  $\underset{\mathrm{A}}{\mathrm{PhCH_2}}\underset{\mathrm{B}}{\mathrm{CH_2}}\overset{\mathrm{H}}{\mathrm{N}}\underset{\mathrm{C}}{\mathrm{CH_2}}\mathrm{Ph}$	1·18 (1·0) (N$\underline{H}$)s 2·68 to 2·81 (3·92) (A, B)s 3·68 (2·08) (C)s 7·18 (10·1) (aromatic)d	3·0 (w) 3·3 (m) 3·5 (m) (doub.) 6·2 (m) 6·7 (s), 6·9 (s) 9·0 (s)

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[a] Chemical shift, ppm relative to TMS; [b] Relative intensity; [c] Assignment; [d] Description of absorption: s, singlet; d, doublet; t, triplet; m, multiplet; [e] IR absorption in microns; [f] Relative intensity: s, strong; m, medium; w, weak; [g] PMR run in D_2O with $(CH_3)_3Si(CH_2)_3SO_3Na$ as reference.

in small pieces to maintain the refluxing of EtOH. (EtOH had to be added periodically to prevent solidification). After the Na was added, the flask was heated, and the EtOH reflux was continued until all of the Na was consumed. The cooled soln was diluted with water and made weakly acidic with conc HCl. The EtOH was then removed by distillation. The ppt which formed when HCl was added redissolved upon removal of EtOH. The soln was made strongly basic with KOH and the ppt recrystallized twice from ether giving white plates. m.p. 117°–118·5° (lit.[15] m.p. 120°). PMR;[16] 1·28[a] (2·08)[b] (NH_2)s,[c,d] 3·98 (1·0) (PhCH—)s; 7·30 (4·85) (aromatic)s. 1,2-Diphenylethylenediamine made by this procedure was not present among the products of photolysis of benzylamine.

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