Registry No.—**1**, 30681-63-1; **2**, 37931-42-3; **3**, 37931-43-4; **4**, 37931-44-5; **5**, 27023-72-9; **8**, 37931-46-7; **10**, 37931-47-8; **11**, 37931-48-9.

Nitrogen Photochemistry. XI. Liquid Phase Irradiation of Primary Aliphatic Amines[1]

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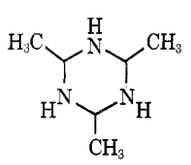
For some time, we have been studying the photochemistry of alkaloids and, as a direct consequence, it has been necessary to resolve some of the problems associated with amine photochemistry. The primary products from the liquid phase ultraviolet (uv) irradiation of several aliphatic amines have been isolated and identified to resolve existing questions on the probable (1) formation of imines and (2) existence of C–N bond cleavage in these photolyses.

Uncharacterized, unsaturated compounds are formed in equivalent amounts to hydrogen generated during the irradiation of hexane solutions of *n*-hexylamine and ethylmethylamine.[2] The irradiation of cyclohexylamine in cyclohexane produces exclusively cyclohexylcyclohexane in molar amounts.[3]

Pouyet reports that the irradiation of primary amines as 2-propylamine, *n*-butylamine, and isoamylamine in hexane provides hydrogen and 1-hexene in approximately equivalent amounts.[4,5] When the irradiation of primary amines is done in water, the corresponding alcohols and ammonia are formed.[4,6] Branching at the α carbon to the amino function enhances the reaction rate in both instances. Esr evidence has been given for presence of $CH_3CH{=}N\cdot$, $CH_3\dot{C}HNH_2$, and $CH_3CH_2\dot{N}H$ during the irradiation of ethylamine in an adamantane matrix while similar irradiations of *n*-propylamine and *n*-butylamine exhibit signals assigned to $RCH{=}N\cdot$ and $R\dot{C}HNH_2$.[7] At 77°K, Hadley and Volman have demonstrated that the irradiation of methylamine with 184.9-nm light gives esr signals for the $CH_3NH\cdot$ radical.[8]

In the vapor phase, irradiation of methylamine gives a trimer of methyl methylenimine, I, in addition to a polymer.[9–13] Mass spectrometric analysis of the gases has demonstrated the presence of a C_2H_5N compound which has been assigned the structure of ethylenimine.[10]



I

Experimental Section

Reagents.—The following lists the commercial sources of the chemicals used: Aldrich Chemical Co., cyclohexylamine, cyclopentylamine; Eastman, *n*-hexylamine, cyclohexylcyclohexane; and Chemical Samples Co., *n*-hexylcyclohexane, cyclopentylcyclopentane. Cyclohexane and cyclopentane were purified by known procedures.[14] *N*-1-(Hexylidene)hexylamine and *N*-cyclopentylidenecyclopentylamine were synthesized by the method of Campbell, *et al.*,[15] Dicyclopentylamine and *n*-hexylcyclohexylamine were prepared by reduction of the corresponding imines with excess 10% Pd/C in ethanol and vacuum distillation.

General Procedure for Products Accumulation Studies.—The irradiations were done in a quartz tube with a ground glass point using a 450-W medium-pressure Hanovia mercury arc lamp. Nitrogen gas free of oxygen was passed into the solution *via* a bubbler for 30 min prior to irradiation. The sample tube and the immersion well containing the lamp were placed in a 13.4 ± 0.1° water bath. Aluminum foil was placed around the upper part of the sample tube to avoid irradiating the vapors. The distance between the quartz tube and the edge of the immersion well was held constant at 3.5 cm. The reactions were monitored using a Beckman GC-5 equipped with flame ionization detectors, Disc integrator, and two 20 ft × 1/8 in. 5% KOH–20% Carbowax–Chromosorb W columns.[16] The cyclohexylamine study was done with 20 ft × 1/8 in. 18% Theed Chromosorb P columns. In order to restrict the number of products to a minimum, solvents with symmetrical molecules were employed.

General Procedure for Products Identification Studies.—The immersion well with lamp was surrounded by a Pyrex jacket containing *ca.* 1.5 g of sample in 300 ml of solvent. The solutions were irradiated for 4 hr with N_2 bubbling through and concentrated; the products were separated by an Aerograph A-700 glpc equipped with a 10 ft × 1/4 in. 5% KOH–20% Carbowax–Chromosorb W column. The product were identified by retention times and comparative nmr and ir spectra except for the air-oxidizable imine, *N*-cyclopentylidenecyclopentylamine. This imine was removed from its reaction solution by a 2 *N* HCl wash or hydrogenated to dicyclopentylamine with 10% Pd/C in ethanol. The latter compound was identified in the usual manner. Ammonia was trapped from the cyclohexylamine and *n*-hexylamine irradiation solutions by passing the effluent gas stream first through a NaCl–ice trap and subsequently through a Dry Ice trap. Ammonia was identified by its characteristic ir spectrum.[17]

Results

The products isolated and identified from the irradiations of cyclohexylamine, cyclopentylamine, and *n*-hexylamine are those represented in eq 1–3. The product accumulation data from these irradiations are illustrated in Tables I, II, and III.

Discussion

The four postulated cleavage patterns resulting from the irradiation of primary amines in the vapor phase are represented in eq 4a–d.[10] Pathway 4a is well ac-

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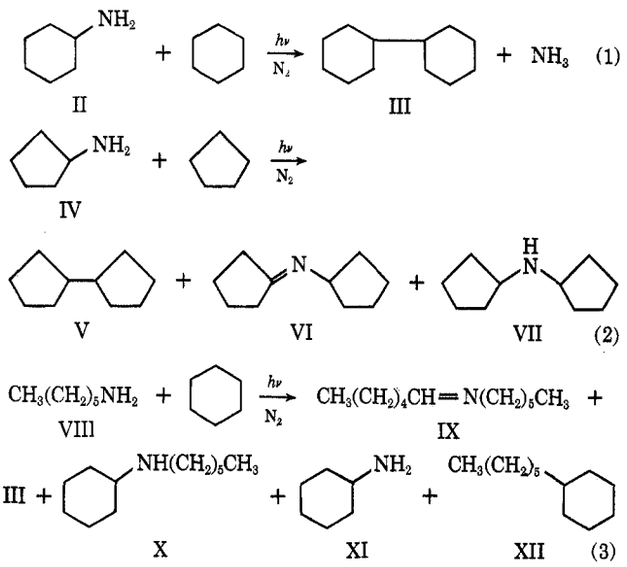


Table I

Photochemistry of Cyclohexylamine in Cyclohexane

Time, min	II × 10^5 *M*	III × 10^5 *M*	ΔII × 10^5 *M*	III/ΔII
0	611			
10	590	18	21	0.85
20	573	39	38	1.03
40	554	75	57	1.31
60	480	132	121	1.09
120	438	182	173	1.05
180	295	193	316	0.61

Table II

Photochemistry of Cyclopentylamine in Cyclopentane

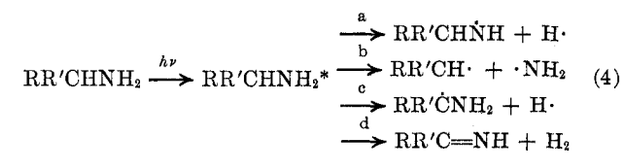
Time, min	IV × 10^5 *M*	V × 10^5 *M*	VI × 10^5 *M*	VII × 10^5 *M*
0	570			
5	546	13	8	7
10	538	19	9	9
20	515	32	21	9
40	445	54	35	10
60	385	77	59	10
120	273	119	115	11

Table III

Photochemistry of *n*-Hexylamine in Cyclohexane

Time, min	VIII × 10^5 *M*	IX × 10^5 *M*	III × 10^5 *M*	X × 10^5 *M*	XI × 10^5 *M*	XII × 10^5 *M*
0	611					
5	573	16	6	7	3	1
10	528	34	8		3	1
20	491	65	17	8	4	1
40	325	92	31		11	2
60	309	116	47	14	15	5
120	244	181	77	14	12	10

cepted; however, 4b is presently relegated to a minor role. There is indicative but not definitive evidence for 4c and 4d.



If pathways 4a–d are functioning, the relative importance of each should be determined in part by the stability of the alkyl radical RR′ĊH. We now wish to report the results of testing this concept. The alkyl radicals of the amines selected have the following order of stability: $C_6H_{11} > C_5H_9 > C_6H_{13}$. The primary radical is less stable than the two secondary ones, and the bond hybridization accounts for the relative stability of the cyclohexyl and cyclopentyl radicals.[18] If the alkyl radical stability idea is correct, cyclohexylamine irradiation solutions should contain more products resulting from C–N cleavage than that of *n*-hexylamine with cyclopentylamine giving an intermediate amount.

The C–N bond cleavage, 4b, is the dominant reaction resulting from the excited state of cyclohexylamine because the sole product in cyclohexane is cyclohexylcyclohexane. Further, the moles of cyclohexylcyclohexane equals the amount of amine decomposed within experimental error; *cf.* Table I. Although Booth and Norrish[2] were unsuccessful in finding ammonia during the irradiation of *n*-hexylamine in hexane, it has been found as a product in gas phase methylamine irradiations,[12] and we were successful in trapping it from the cyclohexylamine irradiation solution. Thus eq 4b, 5, and 6 adequately summarize the latter reaction.

$$\cdot NH_2 + C_6H_{12} \longrightarrow C_6H_{11}\cdot + NH_3 \quad (5)$$

$$2C_6H_{11}\cdot \longrightarrow C_{12}H_{22} \quad (6)$$

In contrast to the cyclohexylamine reaction, the irradiation of cyclopentylamine in cyclopentane produces a considerably different set of products; *cf.* reaction 2. Though cyclopentylcyclopentane is the major product, nitrogen-containing products as *N*-cyclopentylidenecyclopentylamine (VI) and dicyclopentylamine (VII) are also formed in good yields. The imine VI is not reduced in the reaction solution to the amine VII; however, the reverse reaction can and does occur. Consequently, dicyclopentylamine achieves a photostationary state in the reaction solution; *cf.* Table II. Although the irradiation of VII produces a high yield of VI, it is not the principal source of the imine because of the immediate and linear formation of VI during the irradiation of cyclopentylamine.

The appearance of dicyclopentylamine in the cyclopentylamine reaction solution implies that reaction 4a is functioning during the irradiation. It is unlikely that reaction 7 is occurring subsequent to reaction 4c as an alternative to 4a because 4c did not operate during the cyclohexylamine irradiation, and the rate of reaction 7 is expected to be slow since the C–H and N–H bond dissociation energies are nearly the same.[19]

The irradiation of *n*-hexylamine (VIII) in cyclohexane provides the imine, *N*-1-(hexylidene)-*n*-hexylamine (IX), as the major product, *i.e.*, 50% yield at all times measured; *cf.* reaction 3 and Table III. Both alkyl groups of the imine are derived from *n*-hexylamine in accordance with the well-accepted reaction 8.

$$CH_3(CH_2)_5NH_2 + CH_3(CH_2)CH{=}NH \longrightarrow IX \quad (8)$$

The remaining question of whether the imine, $CH_3(CH_2)_4CH{=}NH$, is formed by a two-step process

(18) For the relative reactivity of C_6H_{12} and C_5H_{10} towards Cl, *cf.*, C. Walling and P. S. Fredricks, *J. Amer. Chem. Soc.*, **84**, 3326 (1962).

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involving reaction 4a or a single-step one utilizing 4d can readily be decided by comparing the *n*-hexylamine and the cyclohexylamine reactions. Reaction 4d is expected to more readily occur during the irradiation of cyclohexylamine than with *n*-hexylamine whether one considers the relative bond dissociation energies of the α-CH bonds or the stability of the resulting imine double bonds. Yet imine formation does not occur with cyclohexylamine. Consequently, it appears the reaction of *n*-hexylamine is using reaction 4a.

It is now possible to conclude that N–H bond rupture is the dominant primary reaction of the excited state *n*-hexylamine whereas C–N bond rupture is most important for the excited state of cyclohexylamine. Though less clear, it appears that cyclopentylamine occupies an intermediate reactivity position as expected.

We have no evidence from this work to support the esr observation of Richerzhagen and Volman[7] on the presence of the imine radical >C=N· during the photolysis of primary alkylamines in an adamantane matrix. Since they have presented evidence that this species is generated from the excitation of another radical, we assume the precursor radical is not allowed to build up under the conditions of these experiments as it is in either a matrix or in cold solution.

All the amines of this study have absorption only at the far end of the near-uv range of the spectrum. The absorbance of the pure amines commonly reach 2 at about 240 nm with considerable tailing to about 300 nm when the spectra are obtained in a 1-cm cell. Therefore it is desirable to use quartz irradiation vessels with the full output of the mercury arc to effect these reactions.

Registry No.—Cyclohexylamine, 108-91-8; cyclopentylamine, 1003-03-8; *n*-hexylamine, 111-26-2.

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Proton Magnetic Resonance Spectra of Aromatic *N,N*-Dimethylcarboxamides. Evidence for Hindered Rotation and Anisotropic Effects Caused by Additional Phenyl Rings[1]

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A previous publication from this laboratory[2] reported a large chemical shift difference (42 cps as compared to 10 cps for *N,N*-dimethylformamide) observed for the protons of the amide methyls in *N,N*-dimethyl-9-carboxamido-9,10-dimethylacridane. This seemingly abnormal chemical shift difference was explained on the basis of the preferred conformation of the amide function which places one of the methyls over the aromatic rings in the molecule. It was postulated that, owing to the diamagnetic anisotropic effect of the rings, the trans methyl experiences a long-range shielding effect, the methyl group cis to the carbonyl being unaffected. This then causes the net chemical shift difference to be large. As no report of the magnitude of such a shielding effect caused by additional phenyl rings has yet appeared, here we present a systematic study of the pmr spectra of aromatic *N,N*-dimethylcarboxamides containing up to three fused phenyl rings.

The results are summarized in Table I. The free energy of activation for rotation around the C–N bond ($\Delta G^{\ddagger}$) was calculated by the intensity ratio method.[3] It has been shown[4] that the $\Delta G^{\ddagger}$ values obtained by this method are quite reliable when the coalescence temperatures (T_c) are not too high. Unfortunately, the coalescence temperatures and hence $\Delta G^{\ddagger}$ for the anthracene (**5**) and acridine (**6**) amides could not be obtained, since these were much higher than the upper temperature limit for the solvent employed ($CDCl_3$). Use of a high-boiling solvent such as CBr_4 caused extensive decomposition before the coalescence temperatures were reached.

The pmr spectra of substituted *N,N*-dimethylbenzamides have been studied by Jackman, *et al.*[5] It has been shown that electron-donating substituents decrease $\Delta G^{\ddagger}$ while electron-withdrawing substituents increase it. As a nitrogen atom in an aromatic nucleus is known to be a strong electron withdrawer from the para position, it is expected to cause an increase in $\Delta G^{\ddagger}$. The data in Table I indicate that this expectation has been borne out. The ring-to-carbonyl group conjugation present in *N,N*-dimethylbenzamide is known to be responsible for its low C–N rotational barrier[5] (for example, $\Delta G^{\ddagger}$ for the benzamide[5] is 15.5 kcal mol^{-1} while for the formamide[3] it is 21 kcal mol^{-1}). The observed increase in T_c and $\Delta G^{\ddagger}$ with the increase in the number of phenyl rings (Table I) shows that the additional rings cause a decrease in this conjugation. The most likely explanation of this phenomenon probably lies in the steric interactions between the peri hydrogens of the additional rings and the methyl groups of the amide function. The resulting change in the conformation about the ring-to-carbonyl group bond causes an increase in the dihedral angle and hence reduction in the conjugation. This explanation is supported by the large $\Delta G^{\ddagger}$ (22.5 kcal mol^{-1}) observed for 2,4,6-trimethyl-*N,N*-dimethylbenzamide.[6] Steric factors are clearly seen to be predominant in this case.

In monosubstituted *N,N*-dimethylbenzamides, the values for $\Delta\delta$ increase with $\Delta G^{\ddagger}$ in a somewhat linear manner.[5] This is probably due to the increased rigidity with which the amide methyls are held over the phenyl ring. However, in the case of the amides in the present study, the increase in $\Delta\delta$ is too large to be accounted for by this effect alone. For example, $\Delta G^{\ddagger}$ for *p*-nitro-*N,N*-dimethylbenzamide[5] is 16.4 kcal mol^{-1}, compa-

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