

## Nitrogen Photochemistry. Novel Synthesis of Imines from Dialkylamines

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**Summary** Direct u.v.-irradiation of the secondary amines di-n-hexylamine, dicyclohexylamine and n-hexylcyclohexylamine, in cyclohexane liquid solutions, produces the corresponding imines in preparative yields (89—91%). As a consequence we isolated the imine precursors in excellent yields. This confirms Allan and Swan's postulate that ethylidene-ethylamine was an intermediate in the formation of the products they observed.

TABLE

Product distribution and yields

Reactant	Product	Percent yield (± 5%)	Irradiation time h
Di-n-hexylamine (V)	N-n-Hexylidene-n-hexylamine	89	6
	Cyclohexylcyclohexane	10	
	(V)	2	
Dicyclohexylamine (VI)	n-Hexylamine <sup>a</sup>	11	6
	N-Cyclohexylidenecyclohexylamine	89	
	Cyclohexylcyclohexane	15	
n-Hexylcyclohexylamine (VII)	(VI)	5	6 <sup>b</sup>
	Cyclohexylamine <sup>a</sup>	4	
	N-n-Hexylidenecyclohexylamine	62	
	N-Cyclohexylidene-n-hexylamine	29	
	Cyclohexylcyclohexane	16	
	n-Hexylamine <sup>a</sup>	3	
	(VII)	2	
Cyclohexylamine <sup>a</sup>	4		
	n-Hexylcyclohexane <sup>a</sup>	2	

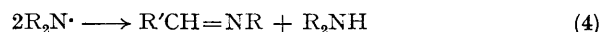
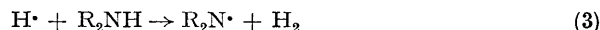
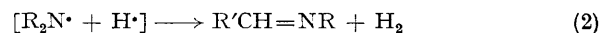
\* Identified by retention time. <sup>b</sup> Optimum yield time was obtained by monitoring the product content *vs.* time.

For some time, we have been investigating the photochemistry of alkaloids and, as a direct consequence, it has been necessary to solve some of the problems associated with amine photochemistry. We now describe a preparative yield photochemical conversion of dialkylamines into the corresponding imines.<sup>1</sup>

Degassed, stirred, 10<sup>-2</sup>M-solutions in cyclohexane of di-n-hexylamine, dicyclohexylamine, and n-hexylcyclohexylamine were irradiated with a 450-W Hanovia lamp. Care was taken to irradiate only the liquid through quartz† while the sample was kept at 18 ± 0.1°. The major products (see Table) were compared (g.l.c. retention times, and n.m.r. and i.r. spectra) with authentic samples.<sup>2</sup>

The results do not contradict those of Allan and Swan<sup>3</sup> who obtained (I)—(IV) from the irradiation of diethylamine since we have examined the solutions at an earlier stage.

The results are in agreement with the accepted cleavage pattern of secondary amines (reaction 1).<sup>4</sup> The low yield



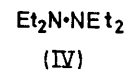
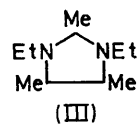
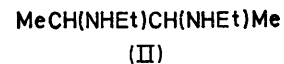
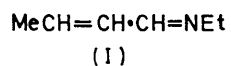
of cyclohexylcyclohexane in the reaction of di-n-hexylamine is an argument in favour of the predominance of reaction (2) after the initial radical formation rather than a combination of (3) and (4). If the radicals escaped from the solvent cage, more solvent radicals would be formed

† Aliphatic amines have only tail absorption in the near u.v. portion of the spectrum.

with consequent enhancement of yields of cyclohexylcyclohexane.

That the hydrogen atom abstraction (2) is governed by statistical considerations is shown by the 2:1 product distribution of the n-hexylcyclohexylamine reaction. The double bond of *N*-cyclohexylidene-n-hexylamine was isomerized only in trace amounts to *N*-n-hexylidene-cyclohexylamine under the reaction conditions.

It is of interest that NH cleavage predominates during the irradiation of dicyclohexylamine whereas CN scission is dominant for cyclohexylamine.<sup>5</sup> Presumably the stability of  $(C_6H_{11})_2N\cdot$  is sufficiently greater than that of  $C_6H_{11}NH\cdot$  because of inductive factors.



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<sup>1</sup> For analogous non-photochemical conversions, see R. W. Layer, *Chem. Rev.*, 1963, **63**, 489.

<sup>2</sup> K. N. Campbell, A. H. Sommers, and B. K. Campbell, *J. Amer. Chem. Soc.*, 1944, **66**, 82.

<sup>3</sup> L. T. Allan and G. A. Swan, *J. Chem. Soc.*, 1965, 4822.

<sup>4</sup> C. H. Bamford, *J. Chem. Soc.*, 1939, 17; G. H. Booth and R. G. W. Norrish, *ibid.*, 1952, 188; S. G. Hadley and D. H. Volman, *J. Amer. Chem. Soc.*, 1967, **89**, 1053.

<sup>5</sup> V. I. Stenberg and C. Niu, *Tetrahedron Letters*, 1970, 4351.