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NITROGEN PHOTOCHEMISTRY VII. CYCLOHEXANE DIMERIZATION AND CYCLOHEXYLAMINE FORMATION VIA EXCITED STATE AMMONIA

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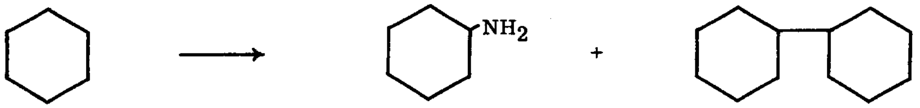
The uv irradiation of ammonia-saturated liquid cyclohexane in quatrz produces two products, cyclohexylamine in a photostationary state and bicyclohexyl, cf. equation 1. Cyclohexylamine, in a cyclohexane solution, can be photochemically converted to bicyclohexyl. The irradiations were done using a 450-watt Hanovia medium pressure lamp.



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The results are consistent with the reported formation of 2-aminopropane during the gas phase irradiation of ammonia and propane[1, 2] and inconsistent with the conclusion that primary amines in hydrocarbon solutions give mainly products resulting from the rupture of the N-H bond[3], i. e., for cyclohexylamine.

Since cyclohexane was purified to give virtually a uv transparent liquid, ammonia has absorption bands in the region of 165-220 nm,[4] and the ammonia-saturated cyclohexane solution exhibits only the absorption bands of ammonia, it is assumed that ammonia is responsible for the initial light absorption which leads to the observed reaction products. A combination procedure was used for the purification of cyclohexane.[5,6]

From the rates of product accumulation curves illustrated in Figure 1, it is apparent both cyclohexylamine and bicyclohexyl are formed in the initial stages of the reaction; and, thus, can be properly classified as primary photoproducts. These curves summarize the activity in the solution up to 0.005% conversion of cyclohexane as determined by flame ionization glpc with a 12 ft Theed column. The compounds were

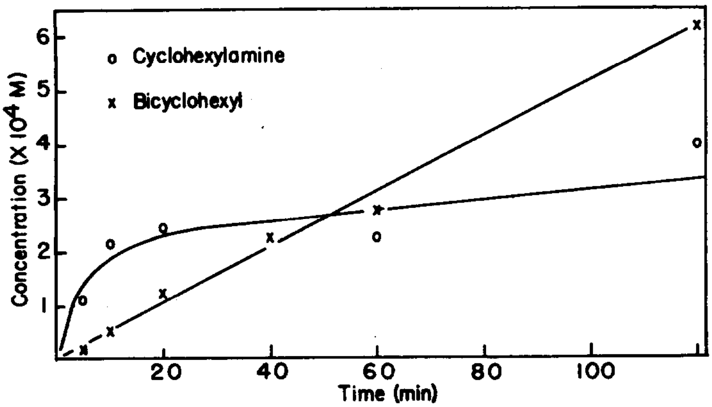

Fig. 1. The irradiation of ammonia-saturated cyclohexane.

identified by comparison to authentic materials. Cyclohexylamine was idenitfied by glpc retention time and its phenylisothiocyanate derivative, and bicyclohexyl by its glpc retention time, nmr, and ir spectra.

It is evident from Figure 1 that cyclohexylamine reaches a photostationary state whereas bicyclohexyl does not. The known photochemical reactivity of alkylamines[3] accounted for this but did not elaborate on the nature of the products formed. As a consequence, cyclohexylamine was irradiated under a nitrogen atmosphere, and it is found to be quantitatively converted to bicyclohexyl (Figure 2).

The above observations are consistent with the following mechanistic scheme:

1. $NH_3 \xrightarrow{h\nu} NH_3^* \rightarrow \cdot NH_2 + H\cdot$
2. $\cdot NH_2 + C_6H_{12} \rightarrow C_6H_{11}\cdot + NH_3$
3. $H\cdot + C_6H_{12} \rightarrow C_6H_{11}\cdot + H_2$
4. $C_6H_{11}\cdot + \cdot NH_2 \rightarrow C_6H_{11}NH_{12}$
5. $C_6H_{11}\cdot + H\cdot \rightarrow C_6H_{12}$
6. $C_6H_{11}NH_2 \xrightarrow{h\nu} C_6H_{11}NH_2^* \rightarrow C_6H_{11}\cdot + \cdot NH_2$
7. $2\ C_6H_{11}\cdot \rightarrow$ bicyclohexyl

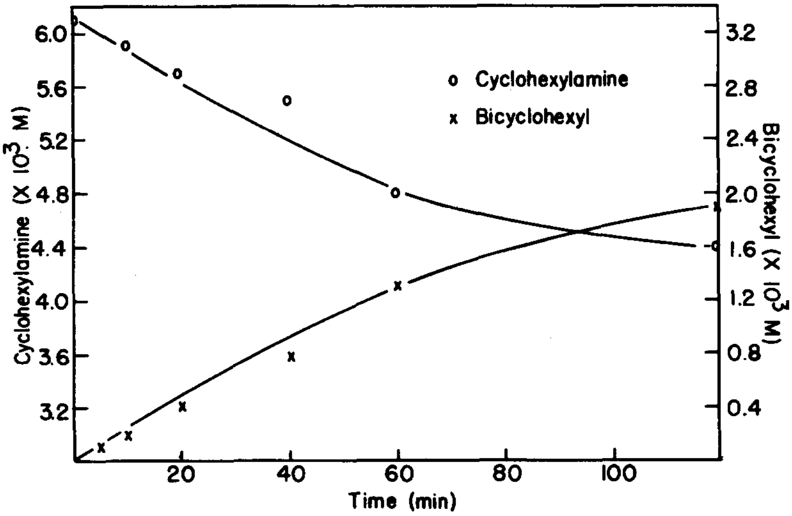

Fig. 2. The irradiation of cyclohexylamine in cyclohexane

In support of this mechanism, hydrogen gas has been observed as a product during the gas phase photolysis of ammonia and propane.[1] The initial step appears well accepted.[3] Reactions 2 and 3 are energetically favorable.[7] To explain the apparent discrepancy on CH *vs.* CN bond cleavage, we suggest that this is due to an energy balance between these two bonds which is influenced by the stability of the alkyl radical.

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